RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XII NUMBER 1

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Treasurer of the Rubber Division, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

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Change in the Time of the Meetings of the Rubber Division at Baltimore

It has been announced that The Rubber Division is to hold its meetings on Wednesday and Thursday, April 5 and 6, with a banquet in the evening of April 5.

The general banquet of the Society has been changed to the evening of April 5, and therefore it has become necessary to hold the banquet of The Rubber Division on Tuesday April 4. For convenience the dates of the meetings have also been changed. The newly announced schedule is:

Sessions (papers, symposium, business meeting)	Tuesday, April 4 Wednesday, April 5
Banquet	Tuesday evening, April 4

New Books and Other Publications

Proceedings of the Rubber Technology Conference. Edited by T. R. Dawson and J. R. Scott. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S. W. 1, England. 7 × 10 in. 1206 pp. $12.00. (Available from Book Department, *The Rubber Age.*)

All of the 103 papers delivered during the Rubber Technology Conference held in London, England, from May 23 to 25, 1938, under the auspices of the Institution of the Rubber Industry, appear in this comprehensive book. Each paper is preceded by a brief abstract and is complete with the discussions which followed the actual presentation. Many of the papers have been corrected and partially revised since being delivered at London.

The papers appear in the book in the same manner that they were given at the Conference; that is, they are divided into subjects and grouped into "sessions." The classifications in which the papers are grouped are: Plantation Subjects; Latex; Chemistry; General Technology; Synthetic Rubber-like Materials; Compounding Materials; Durability; Physics; and Applications. The papers cover almost every conceivable phase of rubber technology, from the physiology of latex-yielding plants to the marketing of manufactured rubber products, and collectively they constitute the most remarkable collection ever published between covers.

In addition to the papers themselves, this book is of value in that it is an accurate report of the Conference proper. Its introduction tells of the preliminary work leading to the Conference and outlines the general conduct of the actual sessions. Other sections give a complete list of the officers, committees, and officials; company and individual supporters; official delegates (by country); those attending; etc. Speeches made at the opening session are included, while reports are given on the various receptions, luncheons, banquets, and visits.

The book includes a list of abbreviations used in literature references, complete to full names and addresses; a numerical index to papers; and an authors' index. A number of trade advertisements appear at the end. [From *The Rubber Age* of New York.]

Encyclopedie Technologique du Caoutchouc. Compiled under the direction of André Bloc and Georges Génin. Published by Revue générale du caoutchouc, 19, Boulevard Malesherbes, Paris, France. In two volumes. 1500 pp. $6^1/_4$ × $9^1/_2$ in. 350 francs. In French only. (Available from Book Department, *The Rubber Age.*)

Compiled under the direction of two of France's leading rubber technologists, this monumental work, the first of its kind to appear since publication of the "Encyclopedie du Caoutchouc" in 1929, published under the auspices of the Syndicat du Caoutchouc, covers the entire field of rubber from plantation to finished rubber products. It is divided into five "books" or sections, three of them in the first volume and the balance in the second. Each section is subdivided into several chapters, each of which is devoted to some specific subject and written by a prominent technologist identified with that subject. Because of the importance of this work, we are presenting the contents of the two volumes herewith, together with the names of the various authors.

Volume I

(with an introduction by J. See)

Book I. Preparation and Properties of Crude Rubber. History of Rubber (G. Génin); Production, Consumption and Prices of Rubber—the Restriction Plan and Future Outlook (G. Génin); Production of Rubber (V. Cayla); Variation in the Properties of Plantation Rubber (G. Martin); Rubber Extracted from Plants other than Hevea (L. G. Akobjanoff); Composition and Physical and Chemical Properties of Rubber and Other Elastic Substances (P. Bary); Changes Which Occur During Vulcanization (P. Bary); Gutta-Percha and Balata (J. N. Dean).

Book II. Modern Trend of the Rubber Industry. One Hundred Years of Progress in the Rubber Industry (P. Alexander); Composition and Properties of Latex (G. Génin); Direct Uses of Latex (G. Génin); Manufacture and Use of Powdered Rubber (B. D. Porritt and R. W. Parris); Preparation and Use of Plasticized Rubber (F. H. Cotton); Synthetic Rubbers and Rubber Substitutes (G. Génin); and Chemical Derivatives of Rubber (G. Génin).

Book III. Control Tests in the Rubber Industry. Chemical Analysis—(*a*) Analysis of Raw Materials, (*b*) Analysis of Vulcanized Rubber, (*c*) Fluorescence, by P. Mensier; Physical Tests of Rubber—(*a*) Control during Manufacture, (*b*) Control and Testing of Finished Products, by A. T. McPherson.

Volume II

Book IV. Preparation of Compounds. Preparation and Use (F. Truchet); Laboratory and Factory Equipment (F. Truchet); Radiovulcanization (H. Leduc); Use and Recovery of Volatile Solvents (G. Génin); Compounding Ingredients (F. Jacobs); Reclaimed Rubber (F. Kirchhof); and Factices (P. Alexander).

Book V. Rubber Products. Pneumatic Tires and Tubes and Solid Tires (J. E. Partenheimer); Rubberized Fabrics (A. Trepau); Conveyor and Transmission Belts (W. Esch); Rubber-Covered Hose (P. Mensier); Rubber in Roads and Paving (F. Jacobs); Flooring and Covering Materials for Buildings (F. Jacobs); Tennis and Golf Balls (S. G. Ball); Artificial Leather and Hides (Y. Cornie); Foam and Porous Rubber; Rubber Thread (R. G. James); Insulated Wire and Insulating Compounds (Domenach); Hard Rubber (Simonin); Bonding of Rubber-to-Metal (Simonin).

Can Closures (F. Jacobs); Rubber Sheet (F. Jacobs); Tennis Shoes and Sandals (J. Panem); Dental Rubber (R. Agrapart); Adhesives and Cements (L. G. Akobjanoff); Paints (H. P. Stevens and S. C. Stokes); Gas Masks (J. Audy); Erasers (W. Esch); Surgical Adhesive Tapes and Plasters (A. Trepau); Seamless Rubber Goods (G. Cany); Packings (W. Esch); Brake Lining (G. Cany); Abrasive Grinding Wheels (H. E. Howard and P. Arnould); Rubber in the Printing Industry (F. Jacobs); and Fireproofing of Rubber (F. Jacobs).

The value of this encyclopedia to the rubber industry can best be appreciated by a study of its contents and by the caliber of the technologists contributing to it. The current work has more than one thousand tables, diagrams, and illustrations, and is complete to author and subject indexes. Unfortunately, its distribution will be somewhat limited since it appears only in French, and it is to be hoped that some day this all-embracing review of developments in the industry will have an English edition. [From *The Rubber Age* of New York.]

Annual Bibliography of Rubber Literature for 1937. Compiled by Donald E. Cable. Published by *The Rubber Age*, 250 West 57th St., New York City. 6 × 9 in. 128 pp. $1.00 (paper bound); $2.00 (cloth bound).

The third "Annual Bibliography of Rubber Literature" is, like the previous issues, of a distinctly practical character. As before, the references are identified by means of a letter-number combination, the various groups being classified under successive alphabetical notations. Thus, accelerators are classified under FA, adhesives under FB, and so on. The preceding two volumes having used up the letters A to E, the present publication covers FA to HY. It should be stated that the references do not constitute abstracts, but constitute a practical method of identifying subject or author. Patents are excluded. In addition to the classification mentioned, there are comprehensive author and subject indexes. Various "tests" which I have made indicate that the subject matter has been well covered, and there would appear to be few, if any, omissions of any consequence. As in previous editions, the classification relates to the name of the author, except where the latter is anonymous, in which case the reference is to the subject matter. [P. Schidrowitz, in the *India-Rubber Journal.*]

Second Report on Viscosity and Plasticity. Prepared by the Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam. Nordemann Publishing Co., Inc., 215 Fourth Ave., New York, N. Y. 1938. Cloth, 7 × 10¼ in. 287 pp. Subject and author indexes. Price, $7.50.

The second report on this subject continues and extends the surveys on various aspects of viscous and plastic deformation which were instituted in the first report published in 1935. The book is divided into six chapters with the following headings and authors: I. Introductory Remarks on Recent Investigations Concerning the Structure of Liquids, J. M. Burgers; II. Viscosity of Liquids in Connection with Their Chemical and Physical Constitution, F. M. Jaeger; III. The Motion of Small Particles of Elongated Form, Suspended in a Viscous Liquid, J. M. Burgers; IV. The Yield Value, R. Houwink; V. Recent Plastometers, C. J. Van Nieuwenburg; VI. Technical Capillary Viscometers, R. N. J. Saal. The reports on which the chapters are based have been subjected to discussion by the full committee. Thus, while the main part of each chapter is the work of the author, many details have been the result of an exchange of opinions.

As indicated by the chapter headings, this volume is devoted chiefly to some of the more basic theoretical aspects relating to this field and reports recent progress in various phases of this work. As the subject matter has an important bearing on the physics of rubber, technologists in the rubber field should find much of interest and value in this volume. Several references to rubber are made in the text. The preface points out that new members added to the committee include R. Houwink and A. van Rossem, who are to work on problems relating to plastic masses (resins, rubber, and artificial products). [From the *India Rubber World.*]

Handbook of Industrial Fabrics. (Second Edition.) By George B. Haven. Published by Wellington Sears Co., 65 Worth St., New York City. 5½ × 8 in. 742 pp. $2.00.

Like the first issue, published in 1935, this latest edition clarifies and extends general information relative to the physical properties of a number of industrial fabrics, including several types pertinent to the rubber field. The section devoted

to A. S. T. M. specifications has been completely revised to jibe with recent revisions. An explanatory chapter on logarithms, slide rules, and nomographic charts has been added in order to place these labor saving devices at the service of textile engineers. Numerous tables have also been inserted in the latest edition to render transformations in weights and measures easier and more direct. Every rubber manufacturer using industrial fabrics should have a copy of this book. [From *The Rubber Age* of New York.]

A. S. T. M. Standards on Textile Materials. Published by American Society for Testing Materials, 260 S. Broad St., Philadelphia, Penna. 6 × 9 in. 330 pp. $2.00.

Fifty-two specifications, test methods, and definitions covering a large number of textile materials are included in this latest annual compilation, prepared by A. S. T. M. Committee D-13 on Textile Materials. In addition, there is a psychrometric table for relative humidity which combines both accuracy and convenience, a section comprising 43 photomicrographs of common textile fibers, a convenient yarn number conversion table, and a glossary of textile terms. Several proposed test methods are also given for information and comment, as are abstracts of ten technical papers presented at meetings of Committee D-13 during the year in symposiums on testing methods and on finishing. For the first time, standards covering colored fabrics (fastness to light), single-ply bleached broadcloth, spun rayon yarns and threads, and other materials are included. [From *The Rubber Age* of New York.]

The Technology of Solvents. By Otto Jordan. Translated by Alan D. Whitehead. Published in England. Distributed by Chemical Publishing Co. of N. Y., Inc., 148 Lafayette St , New York City. 6 × 9¾ in. 348 pp. $10.00.

Not only is this book an English translation of Jordan's "Chemische Technologie der Lösungsmittel," first published in 1932, but it represents a more modern study of solvents since it incorporates a number of references to important publications on this subject, together with particulars of several new products which have appeared since publication of the German edition. In addition, it shows improvement over the original book, in that comprehensive author, subject, and patent indexes, absent from the German edition, are included, making this English translation more convenient as a work of ready reference.

Although various sections of the solvent industry have been treated in the literature, no single volume covered the whole chemical technology of solvents until the publication of this book. Both the author and the translator pay special attention to modern conceptions of the character of solvents and their physical properties. These conceptions are treated in such a manner that they are understandable by the practical technician who may not be too well versed in chemical fundamentals. To this end, strictly mathematical treatment is avoided throughout the book.

The book is divided into two sections—General and Special. Twelve chapters appear in the first section, as follows: Introduction; Physical Properties of Solvents; Solvents for Cellulose Derivatives; Solvents for Resins, Rubber and Similar Binders; Use of Solvents for Extraction Purposes; Plasticizers; The System: Plasticizer + Binder; Physiological Action of Solvents; Recovery of Solvents; Protective Measures; Analysis of Solvents and Lacquers; and The Manufacture of Solvents. The following three chapters appear in the Special Section: Individual Solvents; Plasticizers; Tables.

Brief reference to uses of solvents in the rubber industry is made in various sections of the book. Rubber technologists will be especially interested in references to solvents for rubber and the solubility of rubber in oxygen-containing solvents (Chapter IV), and the discussion of plasticizers for rubber and chlorinated rubber (Chapter VII). [From *The Rubber Age* of New York.]

Toxicity of Industrial Organic Solvents. Summaries of published work compiled by Ethel Browning. The Chemical Publishing Co., of N. Y., Inc., 148 Lafayette St., New York, N. Y. 1938. Cloth, $5^1/_2 \times 8^1/_2$ in. 392 pp. Index. Price, $3.50.

With the increasing use of volatile chemicals which have injurious effects on the health of workers, the need was felt for an investigation which would determine the actual toxic effects of each substance under conditions likely to be met in industry. This book, which represents the first step in this direction, contains conveniently within a single volume the essential information that has been published on this subject. It is intended, in addition to serving as an aid to further research, to assist manufacturers and users of industrial solvents in the solution of their health problems. The chemicals covered in this book are: the hydrocarbons, chloro compounds; alcohols; esters; cyclohexane derivatives; ketones; glycol compounds; carbon bisulfide; pyridine; ethyl ether; and iso-propyl ether. [From the *India Rubber World.*]

The Making and Molding of Plastics. Second (revised) impression. L. M. T. Bell. Chemical Publishing Co. of N. Y., Inc., 148 Lafayette St., New York, N. Y. Cloth, $5^1/_2 \times 8^1/_4$ in. 260 pp. Illustrated. Indexed. Price $5.00.

This book on the production, properties, and uses of plastic molding compositions has been simply written without highly involved technical discussion to provide workers in this industry with an easy and ready means of study. Treatment has been limited chiefly to the more important processes and materials. The first of the book's 12 chapters is devoted to hard rubber, its history, properties, compounding, processing, and uses. Other plastics discussed in detail include bituminous compounds, shellac, phenolformaldehyde resins, ureaformaldehyde compounds, cellulose compounds, and casein. The practical value of the book has been enhanced by the inclusion of chapters on testing and mold design and construction. [From the *India Rubber World.*]

Dyes and Other Synthetic Organic Chemicals in the United States. 1937 United States Tariff Commission, Washington, D. C. 64 pp.

This report presents data on the domestic production and sales of dyes and other synthetic organic chemicals for 1937. The statistics, compiled from returns of 308 companies, are believed to form a complete record of the manufacture of such products. Data for separate items are given in as great detail as is possible without disclosing the operations of individual manufacturers. The booklet reports production of 29,202,000 pounds of coal-tar rubber chemicals, of which 15,166,000 pounds were accelerators and 14,036,000 pounds antioxidants. Statistics on non-coal-tar rubber chemicals are not publishable, since the figures would reveal the activity of individual firms. Copies of the report may be obtained from the Superintendent of Documents, Washington, D. C., at 10¢. [From the *India Rubber World.*]

Buyer's Guidebook of the Chemical Industry. 14th Edition. Chemical Industries, 149 Temple St., New Haven, Conn. $8^1/_2 \times 11^1/_2$ in. 624 pp.

Issued as Volume 43, No. 5, of "Chemical Industries," this 14th annual edition of the "Guidebook" has been completely revised and brought up-to-date. In addition, two new sections have been added—a Specialties Buying Guide and a Trade Name Index. The revised sections include a Table of Back Prices of Chemicals (1933–1937), Trade and Technical Associations, a Geographical List of Chemical Manufacturers, Importers, Distributors, etc., Raw Materials Buying Guide, and Chemical Buying Guide. As in previous editions, it is a well put-together directory of the chemical industry. [From *The Rubber Age* of New York.]

Minerals Yearbook—1938. Compiled under the supervision of H. Herbert Hughes. Published by Bureau of Mines, United States Department of the Interior. 6×9 in. 1340 pp. $2.00. (Obtainable only from the Superintendent of Documents, Washington, D. C.)

Representing the only official record of its kind in the United States, this latest edition of the Minerals Yearbook presents an economic and statistical review of developments in the mineral industry during 1937. It serves to carry forward the annual surveys of mining activities in this country that were inaugurated more than 70 years ago and have been published continuously for nearly 60 years. The book is divided in four sections: Survey of the Mining Industries; Metals; Non-Metals; and Mine Safety. In the section on non-metals are included data on barytes and barium products, carbon black, clays, magnesite and other magnesium compounds, sulfur and pyrites, and talc. It is replete with statistical tables and has 91 illustrations. [From *The Rubber Age* of New York.]

Chemical Engineering Catalog. Twenty-third annual edition, 1938. Published by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. Cloth, 1034 pp. $8^1/_4 \times 11$ in. Illustrated. Index.

The latest edition of this standard reference work for the process industries contains information of several hundred concerns manufacturing engineering equipment and supplies for chemical and related industries including rubber. An innovation in this year's issue is the inclusion of 16 pages devoted to the publication of certain useful nomographs and charts which have been supplied by various commercial firms and educational and research institutions. The volume comprises the following sections: Company Index; Trade Name Index; Equipment and Supplies—Classified Index, Technical Data Section, and Manufacturers' Catalogs; Chemicals and Raw Materials—Classified Indexes of Industrial, Laboratory, and Reagent Chemicals, and Manufacturers' Catalogs; and Technical and Scientific Books Section. [From the *India Rubber World.*]

Chemical Tables from Handbook of Chemistry and Physics. Charles D. Hodgman, Editor-in-Chief. Published by Chemical Rubber Publishing Co., Cleveland, O. 1938. Fabrikoid, $5 \times 7^1/_4$ in. 1416 pp. Index. Price, $2.50.

In answer to numerous requests for a separate book of chemical tables taken from the widely-known "Handbook of Chemistry and Physics" this volume has been published. The new book includes all material of the handbook which is of direct and particular interest to chemists, together with a generous selection of the more valuable tables of general character and features of especial usefulness.

Thus, while much of the material on sound, electricity, magnetism, and optics is necessarily omitted, data on electrochemistry index of refraction and emission spectra are included. In addition to the handbook data, several new tables have been added, including: Melting Point Index of Organic Compounds; Boiling Point Index of Organic Compounds; Potentials of Electrochemical Reactions at 25° C.; Free Energy; Electrochemical Equivalents of the Elements; and Ionization Potentials. Extensive revisions have been made in the following sections: Isotopes; Calibration Tables for Thermocouples; Definitions of Chemical Terms; and Plate and Film Speeds. The page size of the new volume is somewhat larger than the handbook, allowing ample margins and a more convenient arrangement of material. [From the *India Rubber World.*]

[Translated for Rubber Chemistry and Technology from the Revue générale du caoutchouc, Vol. 15, No. 9, pages 326–333, November, 1938.]

The Problem of Making Uniform Crude Rubber and Its Standardization

The problem of attaining uniformity in crude rubber and of standardizing its properties has become of the greatest concern to planters, and at the present time two facts are evident:

1. In evaluating the product which the planter has furnished him, the rubber broker has based his judgment solely on the superficial appearance of the rubber, which frequently has nothing in common with its intrinsic quality.
2. The manufacturer has found frequent cause of complaint in the variability of different lots of rubber which he has purchased and which it has been impossible for him to distinguish by superficial examination.

For these reasons the planters, in agreement with the manufacturers, should welcome the classification of crude rubber into a small number of types based on the physical and chemical properties of the product.

However, considering the variability of rubber at the present time, crude rubber must obviously be uniform before any attempt is made to draw up specifications. As is shown by M. Bocquet in the following discussion, the production of uniform rubber should not require any great efforts on the part of the planters, and if the planters prefer not to change their methods at the present time, it is because their methods are adjusted to the output of commercial sheet rubber, the only kind salable on the open market.

—*The French Rubber Institute*

Discussion

M. Bocquet

DIRECTOR OF TECHNICAL SERVICE OF THE SOCIÉTÉ DES PLANTATIONS DES TERRES ROUGES, SAIGON, COCHIN-CHINA

Commercial Rubber *vs.* Uniform Rubber

It is curious to find that a product as important as rubber, the use of which depends both on its physical and chemical properties, is produced in the form of crude rubber on plantations without any regard for the way in which it is to be used later. It is also curious that to sell this rubber commercially it is necessary only that this rubber be uniform in appearance, regardless of the fact that uniformity of appearance gives no indication of the inherent quality of rubber, except perhaps a guaranty of the cleanliness used in making it, seemingly a point of secondary importance.

A situation like this, which is unquestionably rare in the economic world, can be explained only by the great distances between the producers and consumers, the lack of contact between one another, and the lack of technical control, at least in the past, in the manufacturing operations on the plantations.

The first thing which happened to alter this situation was the shipment to Europe of latex in place of crude rubber. In this way technologists have been able to familiarize themselves with the production of rubber, although it must not be for-

gotten that they have had at their disposal only stabilized latex, which differs from fresh, unstable latex with which the plantations have to deal.

The efforts shown by planters in turning out a product which is satisfactory to the consumer are not new; attempts in this direction have been going on for more than twenty years. If these efforts have so far been unsuccessful, it is perhaps because relatively few technologists have been occupied in the work, or because manufacturers have not agreed on a formula for testing crude rubber, or because they have hesitated to define clearly the properties which they desire, for fear of disclosing manufacturing secrets. Perhaps it is also attributable to the fact that in the past plantation rubber has had less competition from synthetic products than it has today; in other words, because real progress is always preceded by numberless unheralded efforts.

The problem which confronts many planters today is whether it is possible and if so, under what conditions, to produce uniform plantation rubber, preferably of better quality as well. In attacking this problem, the important thing to do is first to study the causes of the variability of crude rubber and to separate these causes into those attributable to variations in the latex and those attributable to variations in methods of production. Next the conditions necessary for the production of the desired commercial quality of rubber should be established, and finally there remains a study of the possibility of turning out rubber better in quality than that of the present commercial product.

Factors Causing Variations in Latex

It will be shown later that the properties of latex have a decisive influence on certain properties of the crude rubber. The factors which have an influence on the properties of latex may be grouped under four headings:

(*a*) Age of the trees.
(*b*) Character of the trees.
(*c*) Method of tapping.
(*d*) Habitat.

Age of the Trees.—Various authors have shown that the latex of *Hevea brasiliensis* varies with the age of the tree. It is also a well-recognized fact among planters that it is easier to produce rubber of good commercial quality by using latex from old trees than by using latex from young plots. Latex from young trees is in general much less stable and consequently requires a greater quantity of anticoagulant.

Character of the Trees.—An examination of the chemical composition of latices from individual trees of an ordinary random plot will disclose notable differences. In the case of a plot of this kind, these differences may merge into an average difference. This is not the case, however, with latex from large areas of grafted monoclones, since in this case an infinite multiplication of a single tree is concerned. Accordingly, there is the risk of the latex imparting to the finished rubber certain characteristic properties.

Method of Tapping.—Another fact equally well known to planters is that the method of tapping has an influence on the character of the latex, particularly on its concentration of dry rubber and its chemical composition. When the ordinary method of tapping, which gives a steady output for a given plot and locality, is replaced by an intensive system of tapping, *e. g.*, when the frequency of tapping is increased or the incision is lengthened, or both changes are made together, the dry rubber content of the latex, normally 35 to 40 per cent, drops to 25 or 20 per cent, and at times to 15 per cent. Conversely, with a change to a more conservative system of tapping, latex containing as high as 45 to 50 per cent of dry rubber is ob-

tained. Likewise, latices obtained by tapping after a long period of rest vary in composition for some time afterwards, and latices obtained by systems of tapping involving monthly periods of rest show periodical variations corresponding to this tapping cycle.

Habitat.—Although it has not been possible to find any direct relation between the soil and the properties of latex, the fact has been established that, in Indo-China, latices from ordinary gray soil are different from those from red basaltic soil, particularly in the greater tendency of latices from the latter soil to coagulate prematurely. Nor can it be said that there is a relation between the luxuriance of growth and the properties of latex, for plots on gray soil as vigorous as those on red soil have furnished latex which has less tendency to coagulate prematurely.

Climate also has an influence on the properties of latex, and slight seasonal variations occur, even in Indo-China, with its rather remarkable climate, except for those particular times such as the wintering period, when the latex is exposed to sunlight, the period when new leaves are growing and absorbing reserves of water in the tree, and the period of abundant rainfall, which may at times dilute the latex considerably by accident.

It is likewise probable that other factors of habitat, *e. g.*, altitude, have an influence on the condition of the trees, and thereby have an indirect influence on the latex from the trees.

It is evident then that, even before he starts to produce rubber, the planter is faced with a variable product in his latex. Some of the factors which cause variability depend on the planter, particularly on his system of tapping; other factors are forced upon him. In the case of a single plantation, where the latex from all plots is bulked, where the method of tapping is standardized, where the latex has little tendency to coagulate prematurely and therefore where little or no anticoagulant is employed, and where the production methods are standardized, in other words, where the chief variable is the seasonal factor itself, this factor is rather small.

Table I gives the results of tests of rubber produced commercially on a plantation in Cochin-China during 1937. It is evident that in this case the manufacturing operations varied but little. The extreme variations from the standard rate of vulcanization are 148 min. and 182 min., or roughly ±10 per cent. This product may be regarded as a uniform rubber.

TABLE I

SEASONAL VARIATIONS IN INDO-CHINA

Tests of Rubber Produced from Bulked Latex on a Plantation in the Terre Jaune Region of South Cochin-China

Cultures of 1911 to 1927

(Test Formula = Rubber 100, Sulfur 10)

Month	Concentration when Coagulated (Percentage)	Amount of Formic Acid (Kg. per Ton of Dry Rubber)	Anticoagulant Compound	Anticoagulant Weight per Ton of Dry Rubber	Smoking Temperature First Day	Smoking Temperature Subsequent Days	No. of Days	Time of Standard Vulcanization (Min.) Sheet 1	Sheet 2	Sheet 3
March	16	5.3	none	...	35–50°	50–59°	4	153	156	158
April	16.5	8.5	Na_2SO_3	5.5	35–45°	45–60°	4	150	152	148
May	18	8.5	Na_2SO_3	5.5	35–45°	45–60°	4	169	139	...
June	17	8.5	Na_2SO_3	5.5	35–45°	45–60°	4	182	179	...
July	18	5.4	Na_2SO_3	5.5	35–45°	45–60°	4	170	150	...
October	18	5.4	Na_2SO_3	5.5	35–45°	45–60°	4	156	172	160
November	18	7.2	Na_2SO_3	2.5	35–45°	45–60°	4	148	160	162

Variable Factors in the Production of Crude Rubber

Of the factors which are responsible for the variability of crude rubber, those concerned with production are by far the most important. They have been studied in great detail by Eaton, Grantham, and Day, whose results were published in 1918 in a book entitled "The Preparation and Vulcanization of Plantation Para Rubber."

The tests were made with vulcanizates prepared from mixtures containing 90 parts of rubber and 10 parts of sulfur. The data include optimum times of vulcanization, tensile strengths, elongations at rupture, and tensile products. Although these remarkable tests were not carried out according to modern ideas, they may be considered quite satisfactory as a whole, since no work so important has been done since that time and since all tests which have been repeated by the present author, using modern accelerators (mercaptobenzothiazole and diphenylguanidine), and measuring stresses at 500, 600, and 700-per cent elongation instead of tensile strengths, have given results in accord with those of Eaton, Grantham, and Day.

It might be added that the present brief work has no pretention to scientific precision in the absolute sense, present facilities making this still unattainable. In the following paragraphs particular attention is paid to the production of sheet rubber.

Bulking of Latex.—It is customary in all modern plantation practice, with an aim to producing uniform rubber, to bulk latices from different plots in bulking tanks of large dimensions, the compartments of which have a capacity as great as 20 to 25 cubic meters. Ordinarily these compartments lead into a single channel which carries the latex to the coagulating tanks, thus mixing in turn the latex from the various compartments. Under these conditions, the latex may be assumed to have been blended to as uniform a state as is possible.

Anticoagulants.—Eaton, Grantham, and Day in their work paid little attention to the effect of anticoagulants. However, they point out that formaldehyde, whether added to latex or used to wet the coagulum before drying, retards vulcanization. This is also true of antiseptic agents such as phenol, mercuric chloride, tannic acid, and boric acid. Likewise sodium bisulfite, employed in the production of crepe, retards vulcanization slightly.

The anticoagulants in current use today, sodium sulfite and ammonia, were not studied by Eaton, Grantham, and Day. According to some investigators, sodium sulfite retards vulcanization. Ammonia on the contrary has a slightly beneficial action, at least during the first hours of storage. Nevertheless, one should not lose sight of the fact that the addition of an anticoagulant necessitates the use of a larger proportion of acid for coagulation. This extra quantity of acid is relatively small in the case of sodium sulfite, but is considerable in the case of ammonia, and it will be shown later than an increase in the proportion of acid has a harmful effect on the quality of the rubber obtained from the latex.

In so far as the use of ammonia is concerned, tests have been made, the results of which confirm what has just been mentioned. In these tests, shown in Tables II and III, the formula adopted by the Crude Rubber Committee of the Rubber Division of the American Chemical Society was used, *viz.*, rubber 200 grams, sulfur 7 grams, mercaptobenzothiazole 1 gram, stearic acid 1 gram, zinc oxide 12 grams, with

TABLE II

EFFECT OF AMMONIA WITH A CONSTANT PROPORTION OF ACID

(6 Kg. per Ton of Dry Rubber)

Weight of Ammonia (Kg. per Ton of Dry Rubber)	Stress at 700-Per Cent Elongation (Kg. per Sq. Cm.)	Hardness
0	104.5	74.5
0.5	112	81
1.5	117	85

a temperature of vulcanization of 126.7° C., and a time of vulcanization of 40 min. This indicates a slight improvement in the rubber.

TABLE III

THE COMBINED EFFECTS OF AMMONIA AND AN ACID

Weight of Ammonia (Kg. per Ton of Dry Rubber)	Coagulating Acid (Kg. per Ton of Dry Rubber)	Stress at 700-Per Cent Elongation (Kg. per Sq. Cm.)	Hardness
0.5	5	113	82.5
1.0	6	112	80.5
1.5	7	104	75

The combined effect of the anticoagulant ammonia and of acid necessary for coagulation was harmful to the rubber. It should be added that to produce commercial sheet rubber free of bubbles, an increase from 0.5 kg. to 1.5 kg. of ammonia per ton of dry rubber ordinarily requires an increase from 5 kg. to 8 or 10 kg. of acid per ton of dry rubber to bring about coagulation. In this case the unfavorable effect of ammonia is especially evident.

Coagulation

Receptacles.—Eaton, Grantham, and Day compared sheet rubber from tanks and from pans and found that the coagulum from tanks was, in general, more porous, dried more rapidly, and its rate of vulcanization was a little slower. This is no longer of much more than historic interest, because most plantations now coagulate in tanks. The tank has the advantage over the pan in that it makes for homogeneity, since it assures a uniform thickness of coagulum.

Concentration of Latex.—All experiments on this problem have shown that the coagulation of latex of high concentration yields rubber which vulcanizes relatively rapidly, and this increase in rate is relatively just as great with mixtures containing powerful accelerators as it is with simple rubber-sulfur mixtures.

Nature of the Acid.—Acetic acid seems to be the most suitable acid for coagulating latex in so far as the physical properties of the resulting rubber are concerned. It can be replaced without inconvenience by formic acid, tartaric acid, oxalic acid, or citric acid. Mineral acids, including sulfuric acid, hydrochloric acid, and hydrofluoric acid retard vulcanization. Alum has a still greater retarding action, even in relatively low percentages.

Quantity of Acid.—An increase in the dosage of acid always has a deleterious effect on the final product. In the case of acetic acid, considerable excess is necessary for the retarding effect on vulcanization to become evident. Formic acid has the same effect as acetic acid, and like acetic acid, it is eliminated by evaporation to dryness. There is danger that tartaric acid, oxalic acid, and citric acid may remain in the rubber. An excess of mineral acid has a powerful retarding effect on vulcanization, an excess of alum still more so.

Machining.—In the case of crepe rubber, machining has a considerable retarding effect on the rate of vulcanization, and it impairs the physical quality of the rubber. This latter effect is attributable, not to the effect of the mechanical work expended on the coagulum, but to the fact that this operation removes not only part of the natural accelerators but also part of the proteins which would otherwise be transformed by biologic activity into accelerators. Consequently, in producing crepe of the highest inherent quality, it is of advantage to make it thick.

As for sheet rubber, any deleterious effects should be attributed, not to the mechanical working which the rubber receives, but rather to the fact that thin

sheets of variable thickness, containing variable proportions of natural accelerators and proteins, are produced.

Washing.—Immersion of the coagulum in water when it leaves the machines, especially when this is done in running water, has a slight retarding effect on the rate of vulcanization.

Draining and Drying.—The effect of prolonged draining, which is in one sense a sort of maturation process, is to increase appreciably the rate of vulcanization by promoting the biologic transformation of proteins into natural accelerators. This effect is particularly notable during the first six or seven days at ordinary temperatures (28–30° C.) protected from light. If the rubber is heated to approximately 50° C., a treatment which resembles a sort of incubation, the effect is further accelerated, and practically ceases on the sixth or seventh day. The accelerators which are formed under these conditions become, at the end of this time, a integral part of the rubber and do not disappear even when the coagulum is machined into crepe. A temperature higher than 50° C. has the same effect as an antiseptic, for it hinders the formation of natural accelerators.

Smoking.—Smoking has a distinct retarding effect on the rate of vulcanization, either because it functions as an antiseptic which combats the formation of natural accelerators biologically, or because it destroys the accelerators themselves. The two effects, heating, on the one hand, and smoking, on the other hand, have opposite effects, and this explains the discordant results frequently obtained with smoked sheet rubber.

In the preceding pages, a diminution in the time of vulcanization has been referred to more often than has an improvement in physical properties, *e. g.*, in tensile strength. The explanation will be evident in the following discussion.

Naturally an increase in the rate of vulcanization is of advantage to the manufacturer, whose presses are thereby tied up for a shorter time for any given product. This shortening of time is therefore of particular interest to him. Even assuming that the time of cure is unimportant, tests show that rubber which vulcanizes rapidly has superior physical properties.

Granted then that the rate of vulcanization is the most important property of crude rubber and that an increase in this rate and control over the rate are of definite advantage, then any efforts directed towards greater uniformity and better quality should mean, first of all, efforts to increase and render more uniform the rate of vulcanization.

Likewise, it should be noted that, in discussing production, we have not mentioned the usual defects of commercial sheet. It should be pointed out in particular that bubbles have no effect on the quality of rubber. This is also true of rust, greasiness, and stickiness.

In the section which follows, the extreme treatment to which latex is subjected at the hands of the planter in order that he may eliminate these defects and produce commercial rubber, irrespective of quality, will be described.

The Problem of Manufacturing Rubber of Commercial Quality

The latex which the planter receives into his factory varies according to the plot, the year, and the terrain. He aims to turn out the greatest possible quantity of rubber designated as No. 1 sheet, which is characterized in the following way:

"The rubber shall be dry, clean, strong, sound, uniformly smoked and ribbed. It shall have no stains, black specks, rust or bubbles."

There is no restriction on the method of production.

Anticoagulant

Irrespective of the conditions under which he receives his latex, whether directly from the tappers or by transportation in carts or tanks, and whatever may be the season, whether rainy or dry, the planter operates under such conditions that the latex arrives in a liquid state at the factory. He combats premature coagulation by the use of anticoagulants, the dosage of which he adjusts during the year and according to the plot. He employs, according to conditions and price, ammonia, sodium sulfite, formaldehyde, sodium hydroxide, sodium carbonate, etc., which differ in their effects on the final product, although in every case the effect is unfavorable. By doing this, the planter reduces to a minimum the quantity of undesired coagulated lumps which he has to convert into crepe, which he is not always equipped to produce, and which usually sells at a lower price than No. 1 sheet; in addition, he reduces the bubbles caused by fermentation in his latex.

Coagulation

Concentration.—After latex is brought to the factory it is blended in bulking tanks. At the same time it is diluted to a concentration of 10 to 20 per cent, according to conditions. The object of diluting it thus is to facilitate decantation, straining, and coagulation. Particularly in the case of unstable latices, it is impossible to produce sheets without bubbles if coagulation is carried out at high concentrations, *i. e.*, above 15 per cent. One result of this reduction in concentration is an increase in the quantity of acid employed, based on the weight of dry rubber. From the practical point of view, the use of greatly diluted latex is inconvenient in that it necessitates a large number of coagulating vessels. In current practice the planter may change the dilution from time to time, *e. g.*, increase it when the latex is relatively stable and when production is very important.

Type of Acid.—With various acids at his disposal, the planter chooses the most economical. Although European plantations, in general, use acetic acid or formic acid, many of the small native planters use sulfuric acid, alum, or proprietary materials which are commercially available. There is no difficulty in manufacturing No. 1 sheet when coagulation is carried out with sulfuric acid or other strong acid.

Quantity of Acid.—It is generally believed that an excess of acid causes bubbles. Even if this may be so when the acid is used in concentrated form, it is never the case in well-organized factories where the acid is added after diluting it to 1 or 2 per cent. In these factories it has actually been found that a deficiency of acid leads to bubble formation by promoting biologic activity after coagulation. For example, whereas 2 or 3 kg. of formic acid per ton of finished rubber is necessary to obtain complete coagulation, 5 to 6 kg. is ordinarily added to avoid bubbles and when the latex is protected by strong alkalies (ammonia or sodium hydroxide), as much as 10 or 12 kg. per ton of dry rubber is added. In other words, four or five times more acid is employed than is necessary for coagulation. Since this acid is very dilute, the latex is diluted still further.

It is evident then that the necessity of manufacturing so-called No. 1 sheet forces the planter to use methods which have decidedly unfavorable effects on the finished rubber, *e. g.*, dilution of his latex and acid in far greater quantity than is necessary simply for coagulation.

Machining.—Machining on a continuous sheeter is now general practice in some of the smaller factories. This method of machining has increased the yields on four hand-operated machines from 100 to 150 kg. per hour to 1000 to 1500 kg. per hour. This has involved two developments. First of all, the coagulum, which in pans is 4 to 5 cm. thick, is in partitioned tanks no more than 2.5 to 3 cm. thick. Secondly,

machining is now carried out in six successive steps in place of four or five. At the same time, there has been an attempt to make thinner and thinner sheets in order to hasten drying. So much for the changes which influence the finished product.

Washing the Sheets.—It is common practice to wash sheets, usually when they leave the battery of sheeters, to eliminate serum substances and any resulting mold from the surface, and thus to obtain better drying and better commercial appearance of the rubber. Cold water, hot water, and even antiseptic solutions, *e. g.*, *p*-nitrophenol, are used for this washing operation. The effect of this washing on the value of the product has already been described.

Draining and Drying.—Draining is an economical way of drying, and is therefore practiced by planters when the biologic activity which ensues does not so affect the rubber that it has to be degraded to a lower quality, *e. g.*, because of the appearance of rust. However, this draining operation has been greatly shortened by an increase in the rate of drying. Modern driers, with careful control, have made it possible to reduce the drying time from 10–12 days to 4–5 days, or even to 2 days. Naturally this reduction has involved an increase in temperature but, in a continuous drier, No. 1 sheet can still be produced even at temperatures as high as 70° C. Naturally all these developments have an effect on the final product. It should be added that to assure easy or automatic operation in drying, some driers are equipped with steam or hot-water heating systems, which make it possible to reduce or eliminate smoking.

The Manufacture of Crepe

In the case of crepe produced from first latex, there are from a production point of view few reasons for any variability. In general, rubber produced in this form is inferior to sheet rubber because of the machining it receives, which removes natural accelerators, and this more than offsets the favorable influence of coagulation at high concentration.

Variability is again evident when one turns to crepe prepared from latex of inferior quality. To produce crepe of uniform color, the planter culls out his inferior product and machines it separately. Now, these inferior types of rubber differ greatly among themselves; some have coagulated naturally (lumps, sernambys, bark scrap, and earth scrap), others have been coagulated artificially (wash water, acid skim); some have been obtained from concentrated latex, others from very dilute latex; some have been exposed to sunlight, solar heat, etc. It is not surprising, therefore, that the method of manufacturing crepe of uniform color gives products which have inherently widely different properties.

Obviously the conditions imposed on the planter of making the best possible commercial rubber, *i. e.*, No. 1 sheet without bubbles and without any faults in appearance, and the modernization of his factories have led him to dilute his latex, to use unnecessarily high proportions of anticoagulant and of acid, to make thinner sheets, to wash the sheets as they leave the sheeters, to shorten the time of draining, and to dry at a higher temperature. All these changes are prejudicial to the inherent properties and to the uniformity of the finished crude rubber. Relatively insignificant variations in the crude latex are magnified by modern methods of manufacture.

The Problem of Making Rubber Uniform and Improving Its Quality

In confirmation of what has just been said, a comparison of rubber from different plantations of a given kind, with modern factories and standardized methods of manufacture, has shown that there are much greater differences between these rubbers than between those from the same plantation where the only variable factor is the seasonal one.

To illustrate this, Table IV shows tests obtained with a 100:10 rubber-sulfur mixture, using two commercial rubbers from different plantations but from plots of the same age and with the same method of tapping; the two rubbers differed, therefore, chiefly in the methods by which they were machined.

TABLE IV

	First Rubber	Second Rubber
Age of plots	1926 to 1928	1925 to 1928
Anticoagulant (kg. of ammonia per ton of dry rubber)	0	2.6
Concentration when coagulated	17%	18%
Formic acid (kg. per ton of dry rubber)	4.6	12
Temperature of smoking	35–55° C.	35–70° C.
Time of smoking (days)	3	3
Time (in minutes) of vulcanization (standard method)		
Sample sheet No. 1	109	195
Sample sheet No. 2	100	198
Sample sheet No. 3	110	183

It should be mentioned that these two examples are not extreme cases; it was impossible to distinguish the two rubbers by superficial appearance. Accordingly, commercial rubbers may vary as much as ±50 per cent in physical quality, in contrast to ±10 per cent in the case of latex.

In the same way we have found differences as great as ±20 per cent in the physical properties of sheet rubber made on the same day in a modern factory which uses blended latex but has not yet standardized perfectly its machining operations. These differences can be explained only by small differences which exist in the manufacturing operations, *e. g.*, between one tank to another or between one smokehouse to another. Such influences may be more important than seasonal influences.

It has been found likewise that, starting with the same latex but changing certain features of the machining operation, the final products differ considerably in their inherent physical properties These differences are evident in the three tables which follow (see Tables V, VI, and VII). In these tables, "A" rubbers refer to rubbers which have been machined under the best conditions, *i. e.*, they are rapidly vulcanizing rubbers; "B" rubbers refer to rubbers of commercial quality No. IX manufactured from the same latex as were the "A" rubbers.

With respect to their chemical composition, the following differences were found between "A" rubbers and "B" rubbers:

	A	B
Water extract (percentage)	1.5 to 2	1 to 1.5
Resins (percentage)	2.5 to 3.5	3.5 to 4
Proteins (percentage)	3 to 3.5	2.8 to 3

The tests of these rubbers lead to the following conclusions:

1. The problem of making rubber more uniform and that of improving its quality are interrelated, since the elimination of factors which cause variability leads in general to an improvement in physical quality.

2. Changes in machining operations will not permit the production of rubber of present-day commercial quality. Present methods of manufacture have been developed with an aim to produce a rubber of commercial quality, and if even one of the operations is changed, No. 1 sheet is obtained only as the exception. It is impossible to guarantee obtaining No. 1 sheet and at the same time a product of uniform and perhaps improved quality.

The argument that the present commercial classification offers the advantage of a rubber of first quality which is guaranteed to be clean and uniform is incorrect and is

out-of-date. It is incorrect, as has already been shown, because such a classification forces the planter to vary his methods of manufacture and as a result to magnify the variability of his rubber. It is out-of-date because no modern factory gives an *a priori* guaranty of cleanliness.

TABLE V

MIXTURE: RUBBER 100, SULFUR 10

Temperature of Vulcanization, 149° C.

Rubber	Tensile Stress (Kg. per Sq. Cm.) 500 Per Cent	600 Per Cent	700 Per Cent	Rupture	Elongation at Rupture, Per Cent	Minutes of Vulcanization
A	20	28	43	116	880	80
B	20	28	42	134	906	146

TABLE VI

CRUDE RUBBER COMMITTEE FORMULA: RUBBER 100, SULFUR 3.5, MERCAPTOBENZOTHIAZOLE 0.5, STEARIC ACID 0.5, ZINC OXIDE 6

Temperature of Vulcanization, 126.7° C.

Rubber	Tensile Stress (Kg. per Sq. Cm.) 500 Per Cent	600 Per Cent	700 Per Cent	Rupture	Elongation at Rupture, Per Cent	Minutes of Vulcanization
A	22.5	39.5	75	190	872	20
	28.5	51.5	101.5	221	850	30
	32	60	115.5	213	815	40
	35	66.5	127.5	210	793	60
	37.5	71	134.5	219	789	80
B	10.5	15	23.5	88.5	979	20
	15.7	24.5	42	145	939	30
	19	30	54	162	902	40
	23	37.5	69	166.5	856	60
	25.5	42.5	79	187.5	856	80

TABLE VII

MIXTURE: RUBBER 100, SULFUR 2.75, DIPHENYLGUANIDINE 0.4, ZINC OXIDE 6

Temperature of Vulcanization, 141° C.

Rubber	Tensile Stress (Kg. per Sq. Cm.) 500 Per Cent	600 Per Cent	700 Per Cent	Rupture	Elongation at Rupture, Per Cent	Minutes of Vulcanization
A	11.5	16.5	27.5	66	866	30
	13.5	21	35	105	906	35
	15	23.5	41	118	893	40
	17	27	48	133	885	50
B	8.5	12	19.5	80	999	40
	15.5	24	43	122	892	80
	17	27	48	130	886	85
	17.5	28	50	61	739	90

The present commercial classification has one advantage and only one, facility of control. The small planter can now judge by eye the commercial value of the product from his factory. Why can he not also do this even if the scheme of classification is changed by establishing an authoritative organization for the purpose? It would seem easy for this intermediary to equip itself at little expense so that it

could check the inherent value of various lots of rubber. Furthermore, are not many contracts even now accepted without the merchandise being seen and merely on faith of previous sales?

It remains to be seen in what way such a change could be brought about.

Two methods for the manufacture of rubber which may be called of "improved" quality and which is at the same time uniform may be considered.

1. The simplest method appears to be to accept the variations which occur in latex and to standardize the manufacturing process; this eliminates in one step the variations which arise during manufacture and which have been shown to be of great importance.

All that is necessary is for the manufacturer to work out in detail by experimentation the conditions under which production on the plantation should be carried out so as to furnish him a satisfactory product. There should be no difficulty in doing this, since this sort of procedure is employed at the present time.

2. A more complicated method, but one which is more precise, is to endeavor to counterbalance the variations in the latex by varying the technic of production. This presupposes a technical education and proper equipment on the part of the planter.

In this latter case the manufacturer has only to state precisely in some form of specification the minimum properties or the allowable tolerances in the physical properties of the rubber which he wishes to purchase.

It seems possible that such a method will become operative in the future, and the present author will be greatly pleased if this discussion leads to a serious consideration of this possibility, and if it aids in the establishment of closer relations between the planters and the manufacturers, with mutual benefit to all.

In the present discussion no mention has been made of the cost of producing uniform rubber, but it follows from what has been said that it is easier to produce rubber of this kind, at no greater expense on a commercial scale, than it is to produce the commercial rubber now being marketed. No consideration is given here to special types of rubber.

If the manufacturer finds that he derives a benefit from this scheme, it will be sufficient for him to pass along a very small part of his profit to the planter, not by way of compensation, but to encourage the planter in his efforts.

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Crystallization of Rubber by Pressure

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The knowledge which has been acquired as the result of studies by means of polarized light and x-rays of the behavior of rubber when stretched has led to the conclusion that rubber is a polyphase system, in which crystals and the liquid phase are in a state of equilibrium which depends not only on the temperature but to a considerable extent on the pressure.[1] This concept is founded on the observation that there is an increase in the crystalline phase after rubber which has been stretched is allowed to rest, and that the anisotropy shows a reversible effect at definite temperatures and degrees of elongation.

Experimental proof of this dependence on pressure has, however, been lacking heretofore, because investigations have been confined to unidirectional stretching, and consequently to pressure in one definite direction. If the conclusion stated above were correct, it would be expected that pressure from all directions would lead to crystallization under conditions whereby it would not otherwise occur. An experiment of this kind was planned at the time of the earlier work, has been in progress since then, and has recently been completed.[2] The results are described in the present paper.

When rubber is stretched, its density increases. From this fact Ruhemann and Simon[3] concluded too hastily that pressure is created when rubber is stretched. Hess[4] too concluded, by assuming a mechanism which could not be proved later, that pressure has an influence on the anisotropic properties of rubber. Experiments to throw light on this phenomenon were, of course, unsuccessful at the time, for the influence of the temperature and of time was not taken into account.

The investigation which is described below was concerned first of all with unvulcanized rubber. The samples were prepared by pouring purified latex onto glass plates and allowing the films to evaporate. From these films rubber strips 1 mm. thick were obtained, and round discs of 10-mm. diameter were cut from these.

The pressure apparatus for the investigation had to be of such a character that it would maintain for long periods a constant pressure and a constant temperature, which were different in each series of experiments. These conditions were fulfilled by the apparatus described below, the pressure equipment of which is shown in cross section in Fig. 1. Two spring-like shells were soldered in a concentric position between two brass plates. The inner shell carried pressures up to approximately 50 atmospheres, the external shell pressures of 2–3 atmospheres. The inner shell was connected with a manometer by a screw cap; the space between the two shells could be exhausted when desired. The ratio of the cross-sectional area of the two shells was so chosen that when the intervening space was completely evacuated, pressures up to approximately 100 atmospheres could be maintained in the inner chamber. By enclosing the pressure apparatus in an electrically heated, thermally insulated container constructed of artificial materials and suitable control instruments, the pressure apparatus could be operated at constant tempera-

tures between 0° and 15° C. An automatically controlled refrigerator set at a low temperature served as a container for the pressure thermostat. This artifice proved of advantage in that it is far simpler to maintain a thermostat at a constant temperature by a controlled supply of heat than by cooling. It was found by experience that careful construction of the chambers and packing the apparatus made it easily possible to operate for a period of a month within the required range of constant temperatures and pressures.[10]

The rubber samples were placed under water in the inner pressure shell.[11] Identical control samples not under stress were placed in the interior of the thermostat on the cover of the pressure chamber. In all experiments, other control samples were placed in the refrigerator.

When the individual samples were to be examined, the chambers were opened to an air supply, the manometer was unscrewed, and after removal of the samples, the chambers were immediately closed again and evacuated.

For examining samples by x-rays, equipment constructed to make a series of pictures was used, and this was cooled at a temperature below 10° C. while the samples were being irradiated. The periods of irradiation, with a screen of 0.6-mm. diameter, were from 5 to 20 min., depending on the distance.

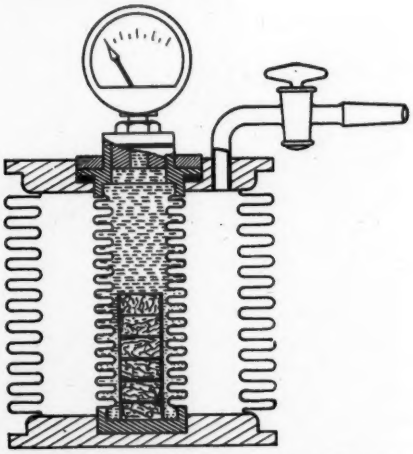

Figure 1—Apparatus for the Crystallization of Rubber with Pressure on All Sides

In the first series of experiments, the refrigerator was maintained at temperatures of 4° to 6° C. One series of samples was maintained under no pressure, the other series was submitted to increasing pressures in the unheated pressure chamber. All the samples which had been subjected to treatment for three months were leathery, turbid, and inelastic. The roentgen diagrams of all the samples, whether or not they had been maintained under pressure, showed Debye-Scherrer rings as well as broad halos. These experiments confirmed past experience that within this range of temperature raw rubber crystallizes ("freezes") even when not subjected to pressure. The experiments also agree satisfactorily with those of Katz[5] and Hauser and Rosbaud,[6] who found Debye-Scherrer interferences upon examination of rubber which had frozen in storage.

Another series of experiments was carried out at temperatures of 8°, 10°, 12°, and 15° C. In this series a pressure of 15 atmospheres was first used. After 37 days under these conditions, the control samples which were stored in an exposed location in the refrigerator at 4° C. showed the x-ray diagram of frozen rubber. After the same length of time, all other samples showed only the halo of an amorphous substance. Not until 71 days did the samples which were kept at 8° under pressure show any change in their x-ray diagrams. Then the broad halo broke and the first weak Debye-Scherrer rings appeared. Accordingly, after 71 days at 8° C. and under a pressure of 15 atmospheres, a part of the fused substance became crystalline. The corresponding samples which had been kept at the same temperature but not under pressure were still completely amorphous after the same length of

time. Further roentgenographs were made after the samples had been kept under treatment for 81, 91, and 131 days. In this case the reflections which appeared at 8° merely increased in sharpness and clearness; there was no change in their character. All other samples which were kept at temperatures above 8° C., whether under a pressure of 15 atmospheres or under no pressure, showed even after 141 days an x-ray diagram with only a bright halo; there was no indication of crystallization. The pressure applied (15 atmospheres) was evidently too low to bring about crystallization at 10°, 12°, and 15° C.

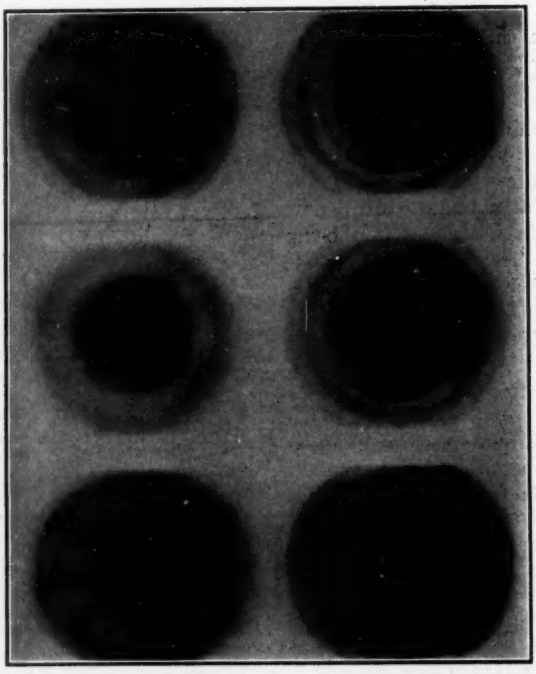

Figure 2—X-ray Diagram of Unloaded Rubber (a) and Rubber under Pressure on All Sides (b) after 127 Days

Ib	7° C., 10 atmospheres' pressure
IIb	8° C., 15 atmospheres' pressure
IIIb	10° C., 25 atmospheres' pressure
Ia	7° C., No pressure
IIa	8° C., No pressure
IIIa	10° C., No pressure

In view of this, a further series of experiments was carried out with an increase in pressure for each increase in temperature, *viz.*, 10 atmospheres at 7°, 15 atmospheres at 8°, 20 atmospheres at 9°, and 25 atmospheres at 10° C.

The results of the tests after 50, 80, and 127 days' treatment are summarized in the following table. In this table a − sign signifies amorphous (a broad halo in the x-ray diagram), a ± sign signifies incipient crystallization (in the x-ray diagram the beginning of a splitting of the halo into weak Debye-Scherrer lines), a + sign signifies progressive crystallization (in the x-ray diagram the halo has almost completely disappeared and the Debye-Scherrer lines are well defined).

Time of Treatment (Days)	7° C.		8° C.		9° C.		10° C.	
	No Pressure	10 Atms.	No. Pressure	10 Atms.	No Pressure	10 Atms.	No Pressure	10 Atms.
50	±	+	−	−	−	±	−	−
80	+	+	−	±	−	+	−	±
127	+	+	−	+	[a]	..	−	+

[a] The chamber in which the experiments at 9° were carried out became leaky, so that this series must be excluded and withheld for further investigation.

The roentgenographs which were obtained after the samples had been treated for 127 days are reproduced in Fig. 2.

The experiments show clearly that the crystallization of rubber is influenced in a fundamental way by the application of pressure on all sides, and that under the influence of such pressure crystallization takes place under conditions where it would not do so otherwise.

However, the temperatures at which crystallization occurs under the pressures in question are not the same as the true melting points corresponding to the particular pressures. This is explained by the fact that after the crystalline phase is once formed, it is stable for an indefinitely long time after the pressure is removed, provided that the temperature does not rise above 20° C. Even after six months, samples treated in this way still showed the same pronounced Debye-Scherrer diagrams as those obtained in the original experiments. After heating the crystallized samples for 2 hours at 15°, 18°, 20°, and 23° C., crystal reflections were still visible at 20° C. by x-rays, but these disappeared between 20° and 23° C. Above 23° C. only the halo of an amorphous substance was recognizable. Consequently, the melting point of the crystalline phase lies between 20° and 23° C. This observation is in good agreement with the data of Hock,[7] who obtained a melting point of 20–23° C. for frozen raw rubber.

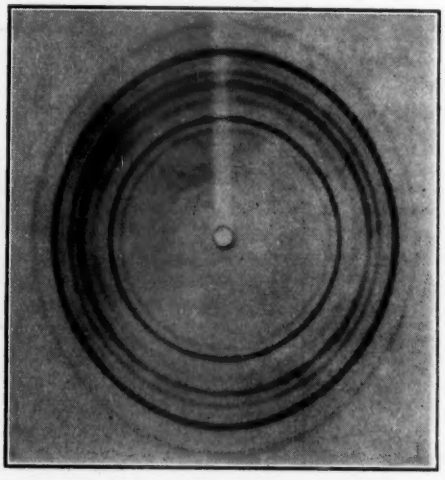

Figure 3—X-ray Diagram of Crystallized Rubber under Pressure on All Sides

As a means of comparison of the x-ray diagram of a sample of rubber, which had crystallized by pressure, exerted from all directions, with the x-ray diagram of stretched rubber, roentgenographs of both samples in the same chamber were obtained. These roentgenographs are reproduced in Figs. 3 and 4. A comparison of the two x-ray diagrams shows that the crystallites formed by stretching have the same elementary cell as those formed by the application of pressure on all sides.

According to these new results it should be possible in principle to bring about crystallization in raw rubber at a temperature of 20° C. without any external influence. However, no spontaneous crystallization at this relatively high temperature has been observed up to the present time. The high-molecular weight and the highly viscous nature of rubber appear to result in an almost infinitely slow rate of crystallization at this temperature, or to prevent the spontaneous formation of

crystal nuclei. Only when the temperature drops to 7° C. or falls below this point, *i. e.*, when there is considerable supercooling, can any crystallization within a measurable time be detected. Consequently, pressure from all directions on the rubber raises this temperature of supercooling.

It must be borne in mind in this connection that crystallization can take place also at higher temperatures provided that the time of the experiment is prolonged correspondingly and, above all, provided that the most suitable pressure for each temperature is applied. That the temperature of crystallization increases with increasing pressure was shown experimentally by the fact that no crystallization took place at 10° C. under a pressure of 15 atmospheres, whereas well-defined crystallization took place at 10° C. when the pressure was 25 atmospheres. The pressure of 15 atmospheres was sufficient to bring about crystallization only at 8° C.

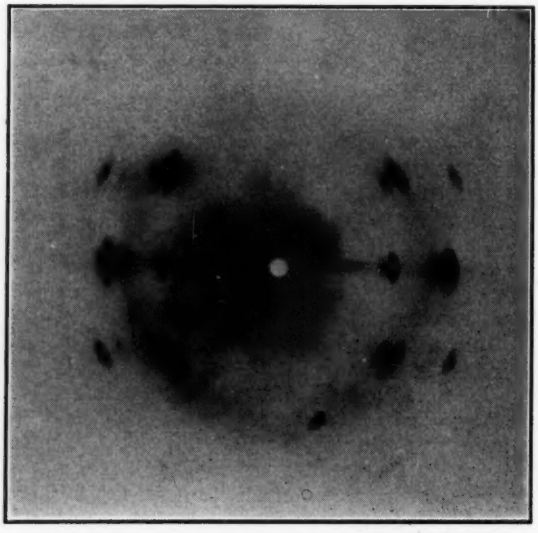

Figure 4—X-ray Fiber Diagram of Rubber at Its Maximum Elongation

The question remains unsettled for the present whether the increase in pressure promotes the formation of crystal nuclei or accelerates the rate of crystallization, or acts in both ways simultaneously. In any case the time factor should never be disregarded in experiments of this kind. There appear to be definite relations between the time necessary for crystallization to take place, the temperature, and the pressure, but quantitative data on these relationships can be had only by further investigations. Up to the present time it has been possible only to establish in a qualitative way the fact that the lower the temperature, the shorter the time for crystallization to take place, and also that at a given temperature the higher the pressure, the shorter the time required for crystallization.

An exact experimental determination of the relation between melting point and pressure was not found to be possible in the present work. However, the conclusion is warranted that the melting point, which has been found to lie between 20° and 23° C. at the ordinary pressure, is displaced towards higher temperatures when the pressure is increased. The observations of Ruhemann and Simon,[3] based

on measurements of specific heats, support this view, as does also the fusion curve obtained experimentally by von Susich,[8] which indicates the elongation at which a fiber diagram appears as a function of the temperature.[9] Pressure vessels which are now under construction are to be used in an experimental study of this problem.

The results described in the present paper show clearly that pressure is a factor of fundamental importance in the crystallization of rubber.[12]

Acknowledgment

The authors owe their thanks to W. Wittstadt for the many ways in which he gave his encouragement and assistance in the present investigation. Appreciation is also shown the Deutsche Forschungsgemeinschaft for the help proffered in carrying out the work.

References

[1] Thiessen and Wittstadt, *Z. physik. Chem.*, **29B**, 359 (1935).

[2] W. Kirsch, *Dissertation*, Berlin, **1937**.

[3] Ruhemann and Simon, *Z. physik. Chem.*, **138A**, 17 (1928). Holt and McPherson, *J. Nat. Bur. Standards*, **17**, 657 (1936).

[4] Hess, Trogus, and Dziengel, *Ann.*, **501**, 62 (1933).

[5] Katz, *Ergeb. exakt. Naturw.*, **4**, 161.

[6] Hauser and Rosbaud, *Kautschuk*, **1927**, 18.

[7] Hock, in Memmler's, "Handbuch der Kautschuk-Wissenschaft," 469.

[8] von Susich, *Naturwissenschaften*, **8**, 915 (1930).

[9] The reader is referred to a forthcoming work on the "Forced and Spontaneous Change in Molecular Arrangement in Stretched Rubber," by Thiessen and Wittstadt.

[10] The apparatus was constructed under the direction of E. Franke in the x-ray workshop of the Kaiser-Wilhelm Institut für Physikalische Chemie und Elektrochemie; the authors are profoundly grateful for this coöperation and the careful way in which the work was carried out.

[11] It was proved in a special series of experiments that water has no influence on crystallization.

[12] Recently it was observed that crystallization takes place in vulcanized rubber within a favorable temperature range. An investigation of the influence of pressure is now in progress.

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Optical and Dimensional Changes Which Accompany the Freezing and Melting of Hevea Rubber

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I. INTRODUCTION

At suitable, low temperatures, unvulcanized rubber loses its elasticity and becomes hard and opaque. Similar changes frequently occur in baled rubber which has been tightly compressed before shipment. It is said to be frozen or "boardy." The phenomenon has been studied by many investigators who have determined changes of volume,[1] softening temperatures,[2] the effects of increasing time of storage at low temperatures,[2] the influence of pressure during freezing,[3] and changes in heat capacity and entropy.[4] These effects have generally been ascribed to a form of crystallization, and x-ray diffraction powder patterns indicate that crystals are present in frozen rubber.[5]

When total rubber is stretched, there are changes of volume and of heat content such as attend crystallization. With x-rays a crystal fiber pattern is obtained. It and the powder pattern obtained with frozen, compact rubber have been shown to indicate similar spacings and are assumed to be caused by the same type of crystal,[6] the differences being ascribed to conditions of orientation.

Dilute solutions of rubber hydrocarbon in ethyl ether yield small crystals of the hydrocarbon when they are subjected to temperatures between $-35°$ and $-60°$ C. for several hours.[7] The optical properties and melting points of these crystals and their x-ray diffraction patterns[6] indicate their identity with the crystals in stretched and frozen rubber. Under the best conditions the crystals appear in spherulitic groupings, the individual needles in each spherulite having optical properties that closely approach those of a uniaxial crystal with negative elongation.[8] The crystals of sol rubber which we obtained,[9] melted between 9.5° and 11.0° C. Crystals of gel rubber[9] melted between $-2°$ and 14° C., but the melting ranges within this interval were not the same for all samples. Numerous observations have repeatedly confirmed the data. About 90 per cent of the rubber in solution may be obtained as birefringent material at $-65°$ C. Temperatures between $-40°$ and $-50°$ C. have been preferred, however, because better crystals are obtained in that range.

Thus crystalline rubber has been prepared in fundamentally different ways—by sustained low temperature, by stretching,[10] by compression, and by separation from solution at low temperatures. It has not been clear whether, in each case, the crystals represented the same solid phase. Since we had previously used the polarizing microscope to determine the behavior of crystalline rubber grown from solution, we decided to extend the observations to frozen and stretched rubbers. By making microtome sections of frozen rubber and its frozen sol and gel fractions, it was possible to determine some optical properties; and by observing the disappearance of birefringence, as temperatures rose, to determine melting points by a technic similar to that which had been used with crystals grown from solution.

II. PREPARING, SECTIONING, AND EXAMINING FROZEN RUBBER

The greater part of the work described in this communication was performed on rubber hydrocarbon purified and separated into ether-soluble and ether-insoluble

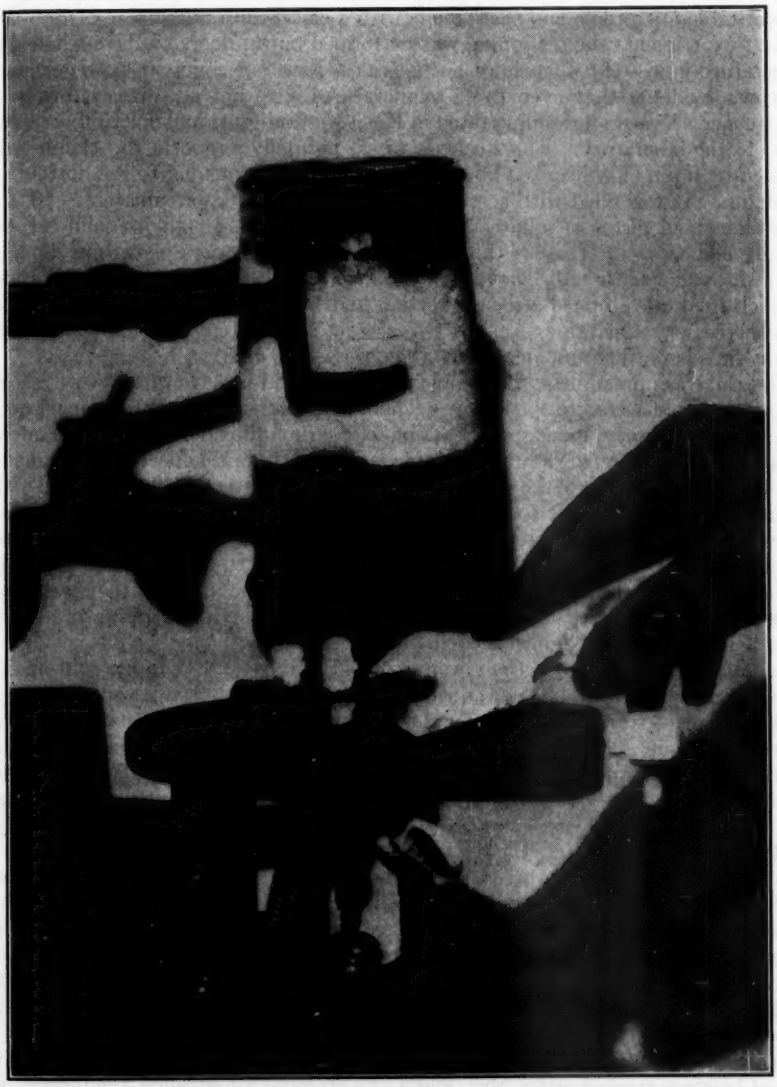

Figure 1—Apparatus for Slicing Frozen Rubber Hydrocarbon

The sample, held in the jaws of the microtome, is surrounded by cold acetone in which are chunks of solid carbon dioxide. From the tin can two streams of carbon dioxide vapor descend on the surface of the sample and the slice after it is cut. The chisel-form knife is used on account of its rigidity

fractions by the methods previously described. The total purified but unseparated hydrocarbon or its fractions, in the form of chunks 0.5 to 1 cm. on a side, were sub-

jected to a temperature of −25° C. for periods of 2 weeks to 3 months. At that temperature oxidation is suppressed. At the end of such periods the pieces had acquired the hardness and turbidity that is associated with the frozen state.

To obtain sections, the chunks of rubber were held directly between the jaws of a Spencer table microtome and slices made with a chisel-form microtome blade. In the first experiments the sectioning was performed out-of-doors on days when the temperature was −10° C. or lower. Such days were not common, however, and there was evidence that even these temperatures were not adequately low. In consequence, the accessories illustrated in Fig. 1 were adopted and operations transferred to the laboratory. The steel pin which normally supports the clamp was replaced by a pin of vulcanized fiber. The trough was cemented to the bottom of the clamp. It was filled with acetone and maintained at approximately −70° C. by adding small pieces of solid carbon dioxide. The can, filled with solid carbon dioxide, had two outlet tubes through which the cold vapors of carbon dioxide emerged, one being directly above the specimen and the other above the position at which the knife stopped after the section had been cut. The microtome blade and all accessory apparatus, brushes, tweezers, etc., were kept surrounded by solid carbon dioxide until the moment when they were to be used.

When all was in readiness, the sample previously held in a Dewar flask with cold acetone was transferred to the clamp. There it was largely immersed in cold acetone and was directly under the stream of cold carbon dioxide. A dozen or more slices were made to prepare a suitable surface and then the critical sections were made —as thin as the behavior of the sample would permit—each section being washed with a brush into the acetone as soon as it was cut. The heat capacity of the knife was such that its temperature did not rise appreciably during the cutting. Occasionally when slicing was difficult, it was thought expedient to interrupt the proceedings and rechill the knife. These sections and the acetone in which they were immersed were then poured into another vessel in which the low temperature could more easily be maintained until needed.

For microscopic study, sections were selected that were as uniform and undistorted as possible. One of them was grasped with a pair of tweezers and by a quick movement transferred to a vessel containing an aqueous solution of calcium chloride at about −20° C. to remove acetone. From this it was transferred to a similar solution in another vessel, placed upon a microscope cover glass, and then covered with another cover glass. The two cover glasses were grasped by the edge with another pair of tweezers and transferred to the wire support of the cold stage illustrated in Fig. 2.[11] Here the sections were studied under the microscope.

In general, sections were easily cut. They could never be made as thin as desired because of a tendency to crumple, and a few specimens were so hard that successful cutting was difficult, but in most instances it was much like cutting across the end grain of a soft wood. It was vitally important, however, that the temperature be kept very low at all times. Otherwise, the outside of the sample would regain its rubberiness and sectioning become impossible. A warning was conveyed when the fresh slice adhered to the edge of the frozen block.

Sections made by the foregoing process were generally about 50 μ thick. When viewed between crossed nicols, they had a fine granular appearance, the individual granules being equidimensional and varying in diameter between approximately 5 μ and 20 μ. A photomicrograph is reproduced in Fig. 3(*A*). It is plain therefore that despite the effort to secure sections as thin as possible, their thickness still was several times the diameter of a particle. In consequence, complete extinction of any part was uncommon. Instead, the granules had high-order polarization colors, the order in each granule changing with the synchronous rotation of the crossed

nicols, as the vibration direction of the first and last particles on any optical path became parallel to the axes of the nicols. Boundaries between adjacent granules were darkened by refraction effects. The entire preparation, by being a complex mixture of small granules of high-order colors and occasional granules in the position of extinction, all separated by dark borders, produced between crossed nicols a general effect of grayness.

When the analyzer was removed, strong refraction effects at the borders persisted, but the interference colors in each granule disappeared. The section still looked very granular, but no noteworthy changes occurred during rotation of the polarizer.

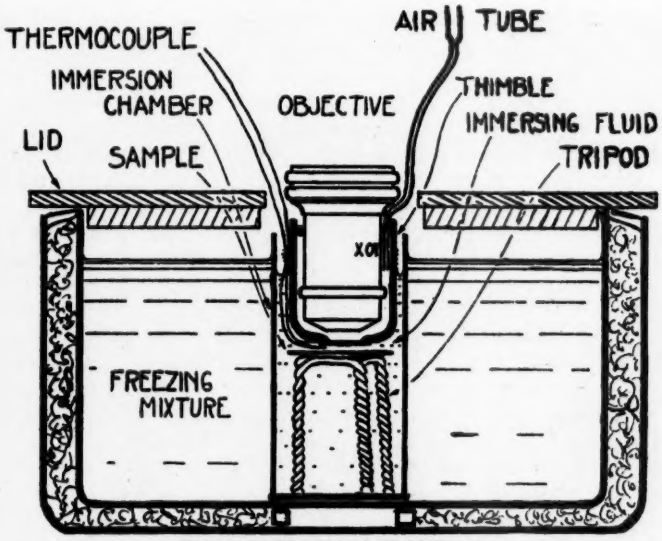

Figure 2—The Simple Cold Stage

Two crystallizing dishes of slightly different sizes were chosen. Except for windows at the center of the bottom, the space between the dishes has been stuffed with rock-wool and the surfaces of the dishes, silvered. The dishes are filled with a freezing mixture. Above the windows rests the immersion chamber made from a glass tube to the lower end of which is cemented a glass plate. This contains immersing fluid and a tripod of bent wire on which the sample rests. The microscope objective dips into the immersing fluid, but is protected by a thimble made from a piece of constricted glass tubing, to the ground lower end of which is cemented a small cover glass. The thermocouple is held in place by being tied with thread to the thimble. The air tube of drawn copper tubing conducts a very slow stream of well-dried air into the space between the objective and the thimble and prevents the formation of frost. The entire apparatus rests upon the stage of a petrographic microscope

Thus, both under crossed nicols and with the analyzer removed, the slices had properties consistent with a section composed of many small crystals, strongly birefringent.

III. MELTING BEHAVIOR OF SECTIONS OF FROZEN RUBBER

1. Unvulcanized Specimens

In general, at temperatures well below the melting point of their crystals, sections which had been prepared from unstrained compact rubber crystallized at sustained low temperatures, exhibited no other birefringence than the heterogeneous birefringence of numerous contiguous granules. At places, however, where the microtome knife had entered a pore in the rubber, then at the edges, or where the section had crumpled slightly, there was an oriented birefringence that had a defi-

nite relation to the direction of cutting. This birefringence was similar to that which was previously noted[7] with crystals of sol rubber grown from a solution. Such crystals yielded plastically, and acquired a new and strong birefringence when they were deformed under the microscope.

In the present work, it was noted that this phenomenon could be greatly reduced if slicing were performed at very low temperatures. The earlier experiments in the sectioning of frozen rubber, undertaken on cold days, out-of-doors, showed the effect rather prominently. In the later work indoors at lower temperatures, well below the melting point of the crystals, the rubber did not yield plastically and

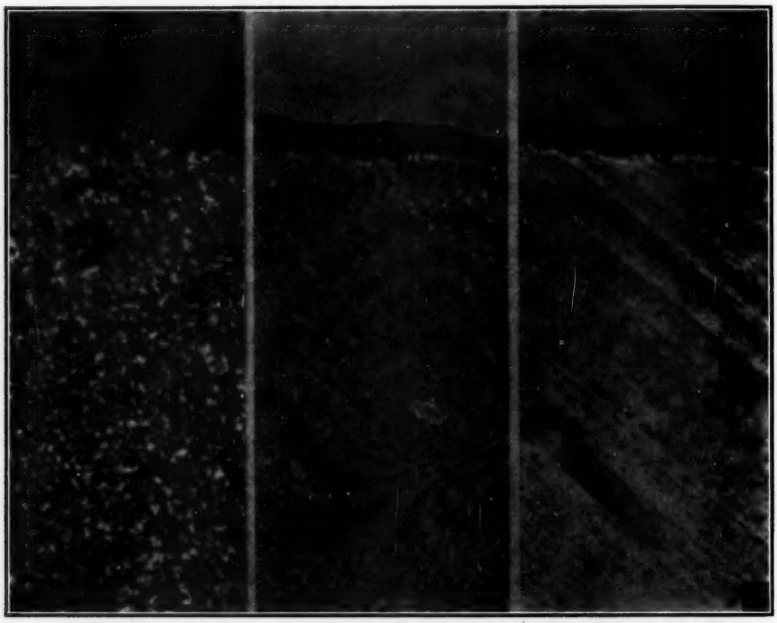

Figure 3—Photomicrographs of Sliced Total Rubber Hydrocarbons

A, view near the edge of a slice of frozen rubber. Temperature about 0° C. Crossed nicols. ×250. All brightness in the field is caused by the birefringence of crystal grains; *B*, same conditions except that polarizer has been removed. Random orientation of birefringent particles causes boundary effects by which crystal grains are seen superimposed upon faint streaks caused by the microtome blade; and *C*, sample at about 15° C. Polarizer removed. Crystals have melted and the grain boundaries between them have disappeared. Streaks caused by the microtome blade are relatively prominent. Between crossed nicols the entire field is black

there was no oriented birefringence. Defects in the cutting edge tended to cause flow and hence new anisotropy. Such effects, however, were not common and did not affect the granular crystallinity.

After the appearance of a slice had been well observed, residual pieces of ice were removed from the freezing mixture, and by passing an electric current through a coiled resistance wire immersed in the bath, the temperature was caused to rise slowly. It was always difficult to determine the precise temperature at which melting of the crystals commenced. Since, except for changes in birefringence, there was no evidence of the melting process until melting was nearly over, and since the birefringence itself had complex causes, it was necessary to observe minutely the first changes of the interference colors. Nevertheless, it is certain that in

nearly all cases some melting occurred at temperatures slightly below the first changes that were noted. During melting, as long as the interference colors were those of superimposed birefracting granules, and therefore composed of interference colors of high order, the changes were difficult to observe and analyze, but as melting neared its end, the polarization colors became much brighter, the transparency of the slice increased rapidly, and refraction effects at the interfaces between granules decreased. Finally, all birefringence related to the granules disappeared and genuine melting of the crystalline rubber was considered complete. Photomicrographs of a melting sequence are reproduced in Fig. 3. At this point some feeble birefringence that was related to the physical history of the sample persisted. The manner in which slices curled and wrinkled after the disappearance of granular birefringence indicated the persistence of strains. Distortions of the rubber, by the act of forming the original piece or of sectioning, showed, as a general, feeble birefringence. Often this did not disappear until well above the melting point (judged by loss of crystallinity) or until there was increasing mobility of the rubber, which is ordinarily so viscous that individual molecules are slow to change their relative positions.

In columns 2 and 3 of Table I is presented a summary of the melting ranges of ether-soluble, ether-insoluble and total rubber hydrocarbons, determined on slices made from frozen compact samples.

The temperature ranges within which the frozen specimens melted are far from the same. The upper and lower limits vary, as well as the ranges of temperatures, and the data offer nothing which distinguishes total, sol and gel rubber. Some specimens began to melt at 4.5°, others at 14°. In one specimen, melting was complete at 8.5°, in another at 15.6°. The temperatures do not agree precisely with those found for unstrained crystals of rubber grown from ether solutions, principally in that the ranges are greater and the reproducibility is less.

TABLE I

TEMPERATURES BETWEEN WHICH MELTING OCCURRED

Specimens Sliced Outdoors at about −10° C.	Specimens Sliced Indoors at about −60° C.	Specimens on Cover Glasses
	Sol	
° C.	° C.	° C.
+9.8 to +12.1 (44.5)[a]	+12.1 to +15.3 (40.7)	+12.1 to +15.0
	+ 6.0 to + 8.5	+14.0 to +15.6
	+ 5.7 to +13.7	
	Gel	
+5.7 to +15.3 (>20)	+10.6 to +15.8 (18.8)	+ 6.5 to +13
+5.7 to +13.8 (>21.7)	— 5.5 to +13.1	+ 5.7 to +15.3
	+ 4.5 to +14.5	+14.0 to +15.1
		+13.5 to +14.9
		+11.1 to +12.2
	Total	
+8.8 to +15.3 (37.3)	+11.6 to +14.4 (17.3)	
	+ 9.5 to +13.5	
	+ 4.5 to +10.5	

[a] Temperatures in parentheses are those at which birefringence of strain disappeared. The birefringences of strain and crystallinity originate in dissimilar causes and, in most cases, are easily differentiated under the microscope.

There were irregularities in the melting ranges of different specimens of frozen rubber, although they were prepared from the same material and were frozen simultaneously. Adjacent microtome sections, cut from any specimen of frozen rubber, melted alike, but sections from widely separated parts sometimes exhibited real

differences. In one experiment an oblong piece of purified total rubber was cut in two parts which were approximately of equal size, and cubical. The two parts were placed in separate bottles and frozen side by side. Samples were sliced from the sides which had been formed when the specimen was cut (*B* and *C* in Table II), and from the sides opposite to them (*A* and *D* in Table II). The data given in Table II were obtained.

TABLE II

MELTING RANGES OF SAMPLES SLICED FROM AN OBLONG BLOCK

Sample	First Changes °C.	Region of Maximum Change °C.	Last Persistance of Granular Birefringence °C.
A	5.0	6.2 to 8.1	9.8
B	4.0	4.5 to 6.9	7.7
C	4.0	4.5 to 6.8	7.6
D	4.1	4.4 to 7.0	7.8
A (repeat)	5.3	5.7 to 8.1	9.0

2. Specimens Partially Vulcanized by Peachey Process

To compare the behavior at low temperatures of unvulcanized and vulcanized rubber, a specimen was surface-cured by the Peachey process. In this method active sulfur is produced at room temperature by the interaction of sulfur dioxide and hydrogen sulfide. The specimen was kept at −25° C. for several weeks, sectioned, and a photomicrograph between crossed nicols was made. (See Fig. 4.) The inner or unvulcanized rubber has crystallized; the outer layers of vulcanized rubber are unchanged except at the edges, which are birefringent, the effect, it was at first supposed, of free sulfur. The edges, however, lost their birefringence at temperatures slightly lower than those at which this occurred in the middle of the specimen. The surface therefore consisted of unvulcanized rubber and not free sulfur. During the vulcanization process, sulfur dioxide probably diffused from the surface before hydrogen sulfide was applied.

IV. MELTING BEHAVIOR OF THIN FILMS OF FROZEN RUBBER

As an alternative method of observing the optical properties that appear with the freezing of rubber hydrocarbon, solutions of the forms of the hydrocarbon in ethyl ether[9] were allowed to evaporate on circular microscope cover glasses. By this means, very thin films were produced. As with the bulk samples, freezing was brought about at a temperature of about −25° C. during 2 weeks, after which the originally transparent films were noticeably murky. They were immersed in a solution of aqueous calcium chloride at about −25° C., transferred to the cold-stage apparatus, and examined between crossed nicols. The general appearance of these samples is represented by the finely grained portions of Fig. 5, and was very similar to that of most of the frozen and sliced samples.

When samples frozen from films deposited on cover glasses were allowed to melt, their behavior was the same as that of sliced rubber, except that there were no birefringences caused by strain that persisted above the temperature of true melting. The melting points of these samples are given in column 4 of Table I. They do not differ significantly from those determined from sections of the bulk specimens.

In several samples of sol rubber prepared as films on cover glasses, there were groups of striking spherulitic clusters. A photomicrograph is reproduced in Fig. 5. Since it was thought that this might indicate a partial recrystallization of the fine-grained portions, the sample was kept for 2 months at −25° C. and examined, and then for 1 month at 0° C., with the hope that recrystallization would be acceler-

ated. Another photomicrograph was made at the end of the 3 months. Since no differences could be observed in prints made before and after that period, it was evident, that no growth had occurred. When the sample was allowed to melt, the rubber film was found to be much thinner at the region of the spherulites. The departure from a uniformly granular appearance, therefore, was caused by fewer nuclei which had formed per unit of area, and because the extent of each crystal in the plane of the film had been correspondingly larger.

The similar properties of frozen rubber in slices and of frozen thin films deposited

Figure 4—Strip of Total Rubber, Vulcanized, Frozen, and Sliced

Crossed nicols. ×25

A strip of rubber was vulcanized by the Peachey process, and then frozen. In the center where the vulcanizing gases failed to penetrate, the rubber has crystallized in the usual way. In two zones on each side of the center zone, where vulcanization was most complete, there has been no crystallization. In thin films along the surface from which it is supposed that the sulfur dioxide diffused before application of hydrogen sulfide, vulcanization has not been sufficiently complete to prevent freezing

from solution on cover glasses established the following points: No important changes in the material were caused by slicing. Solution of total, sol and gel rubber hydrocarbon had not modified the manner of their freezing or the characteristics of the frozen material.

V. EFFECT OF STRESS ON THE FREEZING OF RUBBER

1. Compression

There is a form of boardy rubber which is observed at times in bales of crude rubber that have been tightly compressed before shipment. This is of interest be-

cause it usually persists in the frozen state at ordinary room temperatures or slightly above them, and in this respect is similar to rubber which was frozen for 8 years by van Rossem, and which melted at 37° to 38° C. No crystalline rubber with such melting characteristics has been observed in this laboratory, but the following experiment was performed with the object of producing it. A specimen of gel rubber was used, since in earlier work it had been shown that gel rubber is more resistant to an impressed force than sol. It was placed between two aluminum

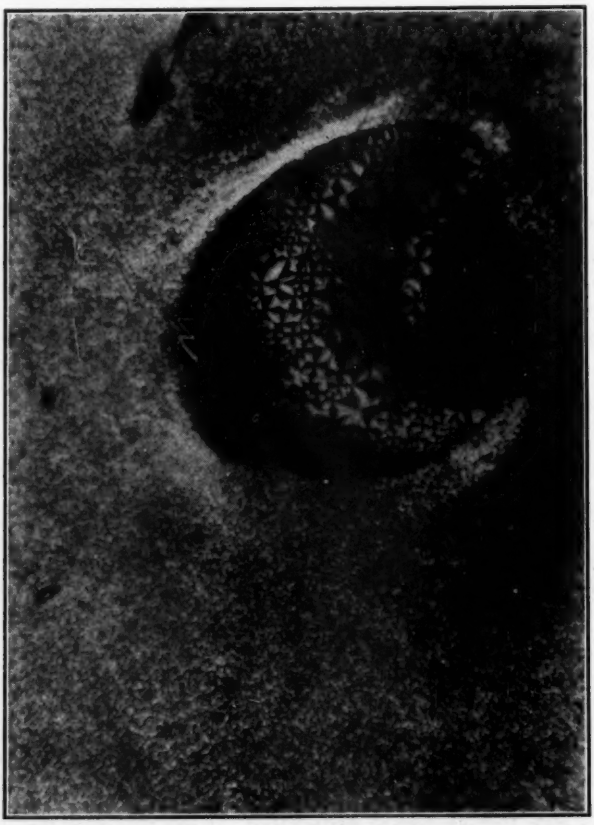

Figure 5—Sol Rubber Deposited on Cover Glass and Frozen
Crossed nicols. ×75
Fine grained portions represent the usual appearance of such samples. The marked spherulitic tendency has occurred in a region where the film of rubber was thinner so that fewer crystal nuclei formed per unit of area

plates, about 6 mm. thick, which were forced together as closely as possible by wing bolts, and immediately subjected to a temperature of −25° C. After 6 months, the specimen was sliced parallel to the axis of compression and examined. The slice had a marked directional birefringence with much extinction when the nicols were parallel and perpendicular to the compression axis. The direction of the highest index of refraction was normal to the direction of compression. Superimposed on this directed birefringence was a granular birefringence that tended to

be parallel to it. By compression, the rubber molecules were oriented to positions which were approximately maintained during crystallization.

Both forms of birefringence disappeared in the temperature range 10.6° to 11.1° C. A birefringence, which, from its position, was no doubt related to the stresses of cutting, slowly disappeared with rising temperature but persisted up to 57.5° C.

Another slice was cut from the frozen material, at a direction 90 degrees from that at which the first slice was made. In this slice also the direction of highest index of refraction was normal to the direction of compression. There was no evidence in either slice of granular, crystalline rubber which persisted above room temperature.

Between aluminum plates the effects were more largely those of distortion than compression. To restrict conditions so that the effects would be primarily those of compression, the following experiment was conducted. A sample of total rubber about 1 cc. in volume was placed in a hole 1 cm. square in a steel block. Steel pistons which closely fitted the cavity were placed above and below the specimen, and the whole was compressed to about 1000 atmospheres between the jaws of a 6-inch screw clamp. After remaining at −25° C. for 2 weeks the specimen was examined. A cubical block of rubber had been formed. It was very hard and exceedingly difficult to slice. Incipient melting was observed at 6.9° C., but the birefringence of the crystalline rubber had not all disappeared until 33° to 34° C. was reached. It was difficult to determine the temperature more exactly as there was sufficient birefringence of strain to obscure that of the granules. This birefringence persisted to 41.3° C. The result is in accord with observations by others[2] of the melting of crude rubber frozen for several years without compression or for several weeks under it.

2. Extension

All available evidence indicates that molecules of rubber are very long. In the course of some observations which were made to test the orientation of birefringent colors by directed strain, a curious effect was observed that probably had its origin in this excessive magnitude of one dimension.[12] For this work strips of crude rubber about 5 mm. wide and 2 mm. thick were used. They were stretched different amounts and nailed to a board. The elongations varied between 20 per cent and the point at which rubber greatly resists further extension. The stretched samples were placed in a cabinet at −25° C. During a few hours, they increased in length about 4 per cent, with the exception of specimens stretched to the point at which further extension was greatly resisted. With them the secondary extension was feeble. The strips rose to form an arc between the points of attachment. The secondary extension was observed with smoked sheet, pale crepe, milled pale crepe, and with smoked sheet that had been swelled slightly by benzene, to remove strains or orientation caused by processing and from which the benzene was subsequently evaporated. The elongation does not occur with unstretched rubber. Stretched vulcanized rubber bands increased in length slightly when kept for several days at −25° C. This is interpreted as an instance in which stretching has fostered the freezing even of a vulcanized rubber. Samples of the product from the reaction between dichloroethyl ether and sodium polysulfide, a Thiokol, also exhibited a secondary extension after 2 weeks at −25° C., whether tested in the unvulcanized or the vulcanized condition.

The piece of smoked sheet that had been swelled with benzene, and from which the benzene had evaporated before the stretching and freezing experiment, was allowed to remain at −25° C. for 2 weeks. It was then sliced, and the sections ob-

served microscopically. They were smooth and very strongly birefringent, the direction of highest index being parallel to the axis of elongation. The multitude of birefringent granules usually observed with the sections of frozen rubber was not present. When the temperature was allowed to rise, slight changes in the degree of double refractions were first observed at −2° C. At +3° C. melting (judged by changes in birefringence) was proceeding rapidly, and at +6° C., after a marked deformation caused by the retraction of the stretched piece, it was complete.

The secondary elongation of stretched rubber may occur at approximately 0° C. and does not require freezing temperatures as low as −25° C. It always disappears, however, on warming to about 10° C., and the rubber resumes its previously stretched condition. This indicates that the elongation is associated with crystallization. The following explanation is suggested.

When stretched or compressed, rubber is forced to flow, its molecules are oriented parallel to the direction of elongation, and when freezing begins a crystal axis is already established. As crystallization proceeds, molecules enter the spacing, the rubber hardens, and presently when a tendency to elongate is asserted, the stresses that produced stretching are neutralized. Then, as more molecules move into the crystalline arrangement, the spacings at right angles to the stretch become less, the long directions of the molecules become more strictly parallel to the axis of stretch, and the strip elongates. Stretched rubber contracts when heated, the well-known Gough-Joule effect. The density of rubber which is chilled while stretched is higher than that of rubber which is chilled without stretching,[13,14] and since the chilling of the stretched rubber is accompanied by an elongation, it is necessarily accompanied by a lateral contraction and a decrease of volume.

When rubber is stretched or compressed there appears to be a movement of whole, or parts of, molecules by compulsion. When a strain orients the molecule so that they are approximately parallel to each other, the movement permits an adjustment of positions so that the rigid spacings necessary for an x-ray diffraction fiber pattern are possible. When stretched, the highest refractive index and, when compressed, the lowest index are parallel to the direction of the applied force. An increased index is an indication either of changed spacing or of orientation of molecules so that their long directions are parallel to the increased index. In the case of rubber, it is evident that the latter phenomenon predominates.

The conditions of melting of stressed and frozen rubber are briefly summarized in Table III.

TABLE III

TEMPERATURE OF MELTING OF SPECIMENS FROZEN UNDER STRESS

Kind of Rubber	Mode of Applying Stress	Conditions of Freezing	Temperature of Melting °C.
Gel	Compressed between aluminum plates	6 months at −25° C.	10.6 to 11.1
Total	1000 atm. applied with piston	2 weeks at −25° C.	6.9 to 33 or 34
Crude	Stretched 20 per cent (secondary increase in length occurred)	2 weeks at −25° C.	3 to 6[a]

Some indications of incipient melting appeared as low as −2° C.

VI. CRYSTALLINITY OF FROZEN AND STRETCHED RUBBER

The granular birefringence of a frozen specimen makes it appear that crystallization has gone far towards completion, but determinations of the density of frozen rubber, as reported in the literature, indicate that rubber when frozen for comparatively short periods of several weeks may be incompletely crystallized. This fact may be related to the varying melting points of frozen specimens prepared under

similar conditions. The density of amorphous rubber is approximately 0.92, whereas that of frozen, unstretched rubber has been reported by several investigators as about 0.95. When stretched and frozen, that is, under conditions which are more favorable to the growth of crystals than when rubber is frozen unstretched, the density increases, and the highest value reported for rubber so treated, 0.965, was obtained by Kirchhof,[13] and was duplicated by Lotmar and Meyer.[14] These authors have calculated from x-ray data that the density of completely crystallized rubber should be 1.02, if there are eight isoprene groups in the monoclinic unit cell. Assuming that 1.02 represents the density of rubber which is completely crystallized, the approximate amount crystallized in frozen rubber would be 30 per cent and in stretched frozen rubber, 45 per cent.

When a block of rubber crystallizes, the medium in which crystallization occurs is, of course, the rubber itself. The ease with which crystallization is initiated is surprising, in view of the low fluidity of this medium. It is probably quickly retarded because chilling must lower appreciably the mobility of molecules, which are admitted to be large. Then too, the mobility necessary for the intimate alignment of molecules in a crystal lattice must be quickly diminished as parts of very long molecules enter into crystalline structures and ultimately impede all further movement. For these reasons, it was hoped that crystallization from a solution of ethyl ether, a medium more mobile than rubber, would induce the maximum number of molecular species to become crystalline. This has not been the case, since when this method is used there is no evidence of crystals which exist unchanged at 25° C. or higher.[7] Our present knowledge of the crystallinity of rubber appears to be far from complete, and deductions drawn from it, therefore, seem subject to reserve.

No doubt exists about the crystallinity of many complex organic compounds, albumin and some vitamins, for example, but there is a curious reluctance by many scientific authors to concede the crystallinity of rubber. The word crystal is frequently used in quotation marks when rubber is discussed, or it is indicated that its use is justified because others have employed it. However, rubber assumes a crystalline state with great facility. This is accomplished merely by stretching it, and its crystallinity is confirmed by x-ray diffraction patterns of stretched and frozen rubber, which indicate the same structure in each. Studies by Thiessen and Wittstadt[15] indicate that crystallization during stretching is influenced by pressure, and that it may be reconciled with the normal process of crystallization which is accompanied by the formation and growth of nuclei.

The superficial characteristic of a crystal, that which attracts the eye, is external symmetry, the regularity and planarity of the bounding surfaces. This external symmetry is only an indication, however, of a more fundamental symmetry, according to which its atoms and molecules are arranged. Crystallinity is defined most rationally in terms of those properties which bring about the symmetry of surfaces. A certain minimum number of atoms or molecules grouped together in a definite pattern is a unit cell. It is the smallest part of a crystal that can contain all spacings and orientations that characterize the crystal as a whole. In an ideal or perfect crystal every part would consist of elements like the unit cell, all strictly parallel to each other and displaced with respect to each other by distances that are precise multiples of the length of a side. From this there results an anisotropy of physical properties. The orderly arrangement causes the diffracted energy of x-rays to follow, by interference, definite paths. With these criteria, crystallized rubber is in complete accord. It has been repeatedly demonstrated that rubber when crystalline produces a characteristic diffraction pattern, which cannot be caused by liquid crystals, as these do not form x-ray crystal patterns.

Usually the unit cell of a crystal contains several molecules. In some substances there are repeated atomic groupings within the molecule. Since these groupings may respond to x-rays as if they were molecules which compose a unit cell, it may happen that the unit cell is much smaller than a single molecule. In rubber the molecule varies in size, but is long, and by some evidence is usually over 500 times as large as the unit cell. Consequently, a rubber molecule may possibly be crystalline in one part and amorphous in another. Perhaps it may simultaneously belong to several different crystalline particles and several groups of amorphous matter. Certainly the crystallinity of rubber is of an unusual type, and differs profoundly from that of a substance like sodium chloride. But each yields a characteristic x-ray diffraction pattern.

REFERENCES

[1] Bekkedahl, *J. Research Nat. Bur. Standards*, **13**, 411 (1934).

[2] van Rossem and Lotichius, *Kautschuk*, **5**, 2 (1929).

[3] Kröger, *Gummi-Ztg.*, **40**, 782 (1926). Carson, *Ind. Eng. Chem.*, **23**, 691 (1931).

[4] Bekkedahl, *J. Research Nat. Bur. Standards*, **15**, 503 (1935).

[5] Hauser and Rosbaud, *Kautschuk*, **3**, 17 (1927).

[6] Clark, Wolthuis, and Smith, *J. Research Nat. Bur. Standards*, **19**, 479 (1937).

[7] The methods of purifying and of fractionating rubber hydrocarbon used in this work and of obtaining discrete crystals from solution have been discussed. *J. Research Nat. Bur. Standards*, **10**, 479 (1933); **13**, 453 (1934).

[8] It is not improbable that the crystals are, in fact, biaxial, although, under the difficult conditions of observation, differences between β and γ, normal to the long axis of the needles, have not been detected.

[9] In the dark, in the absence of oxygen, rubber hydrocarbon can be separated into fractions which are soluble and insoluble in ethyl ether. Ether was used as a medium of separation in earlier work. A separation has been made with petroleum ether, chloroform, and other solvents by different investigators. Whether the same molecular species exist in the two fractions when different solvents are used is not known. In accordance with common usage, the fractions separated with ether are here called sol and gel. The use of these terms does not imply that the sol does not form true solutions. The gel when dissolved may not have the same molecular structure as in latex or as in unmilled crude rubber. Presumably it is insoluble because it has a higher molecular weight than the sol, or a different structure. It is separated from the sol by its insolubility in the absence of light, and in the presence of natural antioxidants which normally protect crude Hevea rubber from oxidation. Light accelerates solvent action. When it is absent, the gel remains undissolved for months. Of the structure of undissolved gel little is known. It may have weak cross linkages connecting molecules which are similar to those in the sol. If that structure exists, the linkages are readily destroyed by light and air. It may possess strong cohesive forces, which are related to the existence of molecules of very long chains. By the breaking of the chains into smaller units these forces would decrease and the hydrocarbon become soluble.

[10] By the application of the term "crystalline" to stretched rubber, nothing is implied except that the atoms assume some form of orderly, spatial arrangement which produces optical effects and x-ray patterns which do not differ in general characteristics from those produced by ordinary types of crystals.

[11] This stage and its equipment have been described in *J. Research Nat. Bur. Standards*, **13**, 453 (1934).

[12] Smith and Saylor, *Science*, **85**, 204 (1937).

[13] Kirchhof, *Kautschuk*, **2**, 155 (1926).

[14] Lotmar and Meyer, *Monatsh.*, **69**, 115 (1936).

[15] Thiessen and Wittstadt, *Z. physik. Chem.*, **29** [B], No. 8, 359 (1935).

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Researches on Rubber and Rubber-like Substances

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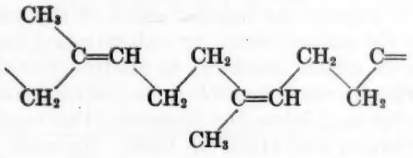
Constitution and Crystal Configuration

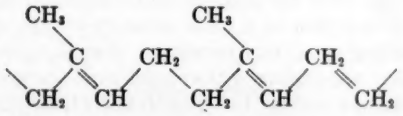
We owe the present generally accepted view of the chain-like nature of the rubber molecule:

$$—CH_2—C(CH_3)=CH—CH_2—CH_2—C(CH_3)=CH—$$

to C. O. Weber.[22] As a result of x-ray investigations, we can today characterize the Weber chain-formula in that in all double linkages the *cis* form is present:



while the *trans* form:

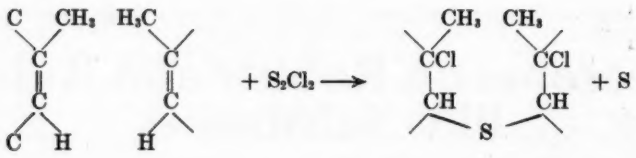


applies to the isomeric hydrocarbon, gutta-percha.[10,14] A third isomer would be a hydrocarbon of the polyprene type, in which both *cis* and *trans* linkages are present. Such chains with a random distribution of *cis* and *trans* bonds occur, probably, in the thermoplastic materials which are obtained when rubber or gutta are heated with substances like $SnCl_4$.[2]

Stretched rubber shows, as was discovered by Katz[7] in 1925, an x-ray fiber diagram. Subsequent investigation of this diagram has not only demonstrated the *cis* structure of the rubber, but provided the following information. Analysis of the diagram[9] shows that in stretched rubber there are two optical antipodes—right-handed and left-handed screws—which compensate each other. In the amorphous state this property of optical activity is lost in that free rotations, hindered in the crystalline state, are restored.

Vulcanization

We owe to Weber[22] not only the present view of the structure of rubber, but also, to some extent, the basis for the present views regarding vulcanization. While it was at one time largely assumed that the sulfur was only loosely adsorbed, Weber showed that actually the sulfur went into chemical reaction with the polyprene chains, although he certainly could not state the type of reaction concerned. A little amplification may therefore be of interest at this point. As has been shown about nine years ago,[14] the reaction of rubber with sulfur chloride S_2Cl_2 (cold vulcanization) corresponds exactly with the well-known mustard-gas synthesis from ethylene and sulfur chloride:



Thus in cold vulcanization one atom of sulfur is liberated from each molecule of sulfur chloride. Recently Meyer and Hohenemser[12] have been able to identify the free sulfur and show that the sulfur is set free in the amorphous form, insoluble in organic solvents.

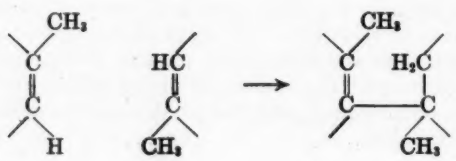
Meyer and Hohenemser have also contributed to the explanation of the chemical processes concerned in hot vulcanization. They were able to show that thioether linkages are present in hot-vulcanized rubber, and that methyl iodide can react additively with these. The methyl iodide number of the vulcanized rubber is a direct measure of the sulfur bridges it contains.

How then are we to explain the peculiar effect of this sulfur reaction on the physical properties of the rubber, which on vulcanization becomes insoluble, less easily swollen, and shows greater resistance to plastic deformation?

The effect is immediately comprehensible if the chemical formulas are considered morphologically. As far as I know the literature, this method of consideration was proposed first by Meyer and Mark[14] in 1928. The main valency chains of the rubber are to be regarded as long threads, which can separate from each other in suitable solvents and slide over one another under mechanical stress, *e. g.*, tension. If the chains are linked together to a loose network by the sulfur bridges, only a limited amount of swelling agent can penetrate, that is, up to the point at which the net is fully stretched; the sliding of the chains over one another under mechanical stress ceases. Processes similar to vulcanization take place also in other systems comprising large molecules, which processes can be similarly described as net-formation; for example, the effect of chromium salts on skin, in which the collagen chains become linked together, the formation of insoluble bodies from protein and formaldehyde, etc. We shall see later that in certain biological substances, *e. g.*, muscle, netted systems occur along with the unnetted ones, determining their plastic and elastic properties.

Now sulfur, as is well known, is not the only substance which can bring about vulcanization. Vulcanization can be effected by benzoyl peroxide, and also by certain physical treatments, *e. g.*, high-frequency currents. In addition, it was shown recently by Ferri[2] that ultra-violet light can cause vulcanization in absence of every trace of oxygen; subsequently it was shown that visible light in presence of iodine has a vulcanizing effect. Vulcanization of this kind is doubtless caused by the formation of cross linkages between carbon atoms of different chains—in this instance, direct C—C bonds.

The double bonds become activated and unite, as in polymerization, with a double bond of a neighboring chain.



The chemical process involved in this kind of vulcanization is the same as in the polymerization of styrene or other ethylene derivatives; such reactions are known to be catalyzed by light and peroxides.

Netted systems can be reconverted into the original soluble and swelling substances if the bridges which have been introduced can be removed. This is possible with chrome leather, from which the chromium can be extracted with oxalic acid and the skin re-formed. With rubber this is not possible, as the —C—S—C- grouping is not easily opened up. A similar effect is achieved, however, by cutting the net in other places, *i. e.*, in the carbon chains themselves. This can be done by heating (cracking), and it is to be assumed that such cracking takes place when rubber is "regenerated" by means of a treatment at a higher temperature.

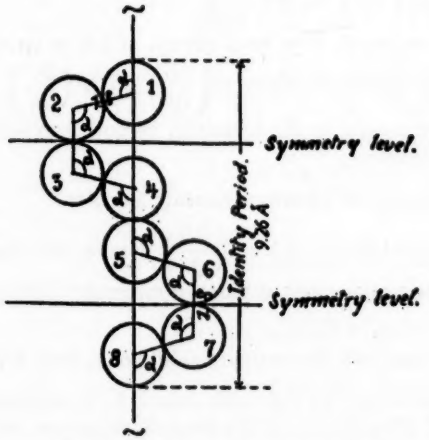


Figure 1—Arrangement of Atoms in the Elastic Sulfur

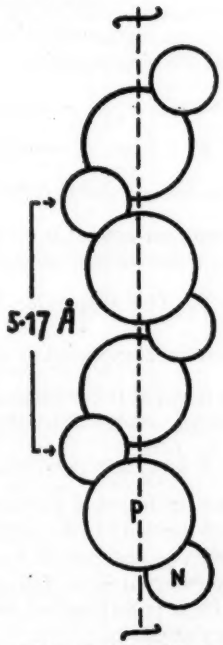


Figure 2—Probable Arrangement of the P and N Atoms in Polyphosphonitrilic Chloride

The Problem of the Elasticity of Rubber

The most striking property of rubber is its high and reversible extensibility. Probably every rubber chemist has tried at one time or another to solve the problem of the reason for this property. Is the restoring force due to the forces of attraction between the molecules, or to other factors? This question has been the object of researches in our laboratory since 1931; they have led to a theory of the elasticity of rubber, upon which I should now like to enlarge.

Rubber is by no means the only substance which shows this characteristic elasticity. We are acquainted with similar properties in polyvinyl alcohol, polyethylene disulfide, as well as with plastic sulfur and the curious mineral rubber discovered by Stokes[20]: polyphosphonitrilic chloride. It was known that some of these substances are built up, like rubber, of very long chain molecules. But the constitu-

tion of plastic sulfur and of polyphosphonitrilic chloride was not elucidated until recently; this elucidation was achieved thanks to the property of both substances giving crystal interferences when stretched, from which the constitution could be deduced.[13,15]

Figures 1 and 2 show the systems of atomic arrangements in sulfur and polyphosphonitrilic chloride, respectively. In both substances there are long chain molecules along the direction of extension, so that we can say that in all probability there are chains of main valency in all substances which possess rubber-like elasticity. The chains may, as in sulfur and unvulcanized rubber, be long free chains, but they may also become joined together to a loose network.

On what, then, does the tendency of the stretched main-valency chains to shorten themselves depend? In order to answer the question as to the nature of the restoring force, let us divide the force, which is exerted during isothermal contraction, into its two components—the change in internal energy and the change in entropy—in the following equation:

$$K = \left(\frac{\partial F}{\partial l}\right)_T = \left(\frac{\partial E}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T$$

where K = force, F = free energy, l = length, E = total energy, and S = entropy.

If we can succeed in determining the above two terms $E\left(\frac{\partial E}{\partial l}\right)$ and $T\left(\frac{\partial S}{\partial l}\right)$, we shall gain an insight into what is happening in the molecule, as both expressions signify quite definite molecular phenomena.

The Molecular Interpretation of Thermodynamic Results

From the standpoint of the mechanical theory of heat $\left(\frac{\partial E}{\partial l}\right)_T$ denotes the change in the internal potential energy between molecules or parts of molecules during an isothermal change of length.

1. If $\left(\frac{\partial E}{\partial l}\right)_T$ is positive, as is the case with an ordinary solid body, then during contraction forces of attraction are satisfied, and the work done is to be attributed at least partially to the saturation of these forces. This means that atoms, which had been pulled out of the position of least potential energy (potential trough) by the external force, fall back into this position. The atoms may in such a case have been pulled out of their potential trough only by the deformation of the valency angle.

2. If $\left(\frac{\partial E}{\partial l}\right)_T$ equals zero, the work done during contraction is to be attributed to the increase in entropy.

The entropy is related to the probability P by the equation:

$$S = R \log_e P$$

P provides a measure of the possibilities of movement and rearrangement open to the kinetic units. An increase in entropy means a transition from an ordered, less probable condition to a more random and more probable arrangement under the influence of thermal motion.

It may be said that thermal motion alone causes contraction, if ∂E equals zero.

3. If $\left(\frac{\partial E}{\partial l}\right)_T$ is negative (*i. e.*, ∂E is positive during an isothermal contraction), the tendency towards rearrangement into a less ordered state is so great that, during isothermal contraction, there is actually more heat absorbed than work given

out. The latent heat absorbed is closely akin to the heat of fusion (since dissociation and evaporation are excluded).

Experimental Method

As a method for determining the above two terms, we chose the determination of the temperature coefficient of the restoring force at constant length, which is best measured by means of the Polanyi extensometer. For this purpose samples must, of course, be chosen which are in equilibrium with the stretching force, *i. e.*, with which the force at constant temperature does not change with time, or with which there is no creep. Under these conditions the following equations hold:

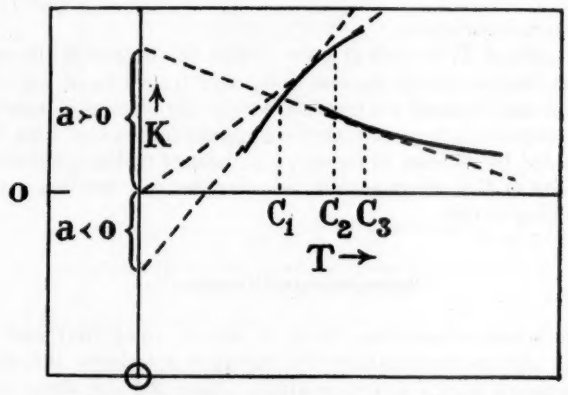


Figure 3—Graphical Determination of E and S

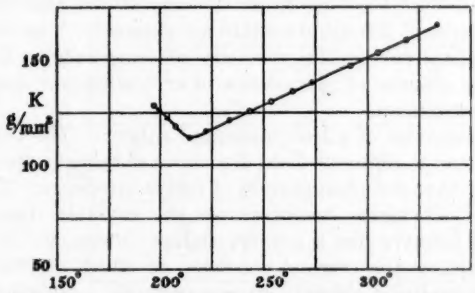


Figure 4—Stress-Temperature Curve of Rubber Vulcanized with 7 Per Cent S

$$K = \left(\frac{\partial E}{\partial l}\right)_T + T\left(\frac{\partial K}{\partial T}\right)_l$$

and

$$\left(\frac{\partial K}{\partial T}\right)_l = -\left(\frac{\partial S}{\partial l}\right)_T$$

Within a small temperature range K can be expressed as a linear function of T (*i. e.*, the curve can be replaced by its tangent):

$$K = a + bT$$

where

$$a = \left(\frac{\partial E}{\partial l}\right)_T \text{ and } b = \left(\frac{\partial K}{\partial T}\right)_l = -\left(\frac{\partial S}{\partial l}\right)_T$$

From this the following deductions can be made:

If, within a given range, K varies in proportion to the absolute temperature, *i. e.*, $K = bT$, then $\left(\frac{\partial E}{\partial l}\right)_T = 0$; hence an isothermal contraction or stretching is not accompanied by any change in E. If $K < bT$, *i. e.*, $\left(\frac{\partial E}{\partial l}\right)_T < 0$, this means that E increases during isothermal contraction, while if $K > bT$, *i. e.*, $\left(\frac{\partial E}{\partial l}\right)_T > 0$, E decreases during such contraction.

If we plot K against T, we can at once deduce the nature of the elastic force: if at a point the tangent passes through the origin (curve C_2 of Fig. 3), then the work done at an infinitesimal contraction equals the change in entropy; if the tangent gives a negative intercept with the ordinate (curve C_1), then the contraction is accompanied by increase in energy, *i. e.*, heat of fusion is absorbed. So by mere observations of the thermoelastic behavior we can see if a crystallization occurs on stretching or not.

Experimental Results

In Fig. 4 the stress-temperature curve of rubber vulcanized with 7 per cent sulfur is shown. At low temperatures the rubber is not elastic and shows the behavior of an ordinary solid; at temperatures above 20° the stress is practically proportional to T. Consequently, no crystallization in stretching or fusion on contraction occurs; indeed, the x-ray investigation confirms this statement.

In Fig. 5 some curves of polyvinyl acetate are shown.[19] The substance is solid below 70°, and acquires rubber-like elasticity at temperatures higher than 70°. The curves show the absence of phenomena of crystallization, and the x-ray evidence supports this statement.

Fig. 6 shows the behavior of a less vulcanized rubber. The curve obtained by raising the temperature is different from the curve obtained on cooling. The ascending curve shows that the phenomenon of fusion interferes. This is confirmed by x-ray evidence. At higher temperatures the crystals disappear, and the rubber when cooled behaves like a non-crystalline substance: it is undercooled, and only slowly acquires the original condition in which crystalline regions are present. Polyphosphonitrilic chloride gives a perfectly analogous curve (Fig. 7).

In all these cases the retractive stress is thus of a fundamentally different kind from the elastic stress in a strained crystal or in strained glass, the atoms of which are pulled, by stretching, out of their potential trough into positions of higher energy. During elastic deformation of rubber and rubber-like substances within large ranges of temperature and elongation, the molecular arrangement becomes, as a result of stretching, more regular through orientation and therefore thermodynamically less probable. The thermal motion then again restores the unordered state of greatest probability as soon as the external force which produces the deformation allows this.[1,6,17]

The tension of stretched rubber is thus closely related to the pressure of a gas: both are due to thermal agitation, both are proportionate to T, if crystallization or condensation does not occur.

The Rubber-like State of Aggregation

According to the above, contraction arises from the tendency of the ordered system to change into a less ordered one. Hence the disorientation is not possible without macroscopic contraction; this forces us to the assumption that atomic

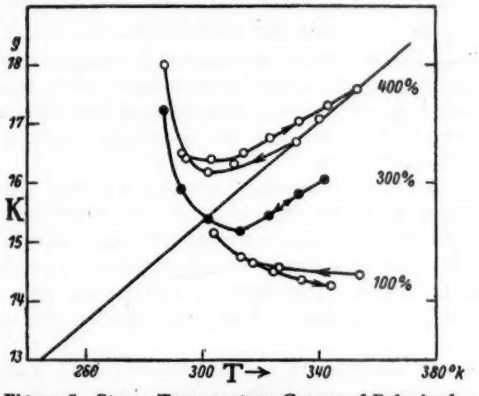


Figure 5—Stress-Temperature Curves of Polyvinylacetate at Different Elongations

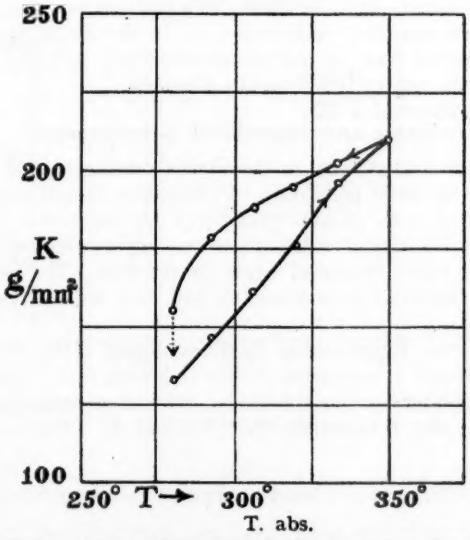


Figure 6—Stress-Temperature Curve of Low Vulcanized Rubber

groups in the oriented state cannot disorientate themselves as do dipoles of a liquid, oriented by an electric field, by disappearance of the field. They must be consequently linked together by strong bonds in the direction of stretching. From this it follows that the rubber-like body is built up of chain molecules. The process of orderly arrangement consists in the stretching out and parallel orientation of

these chains. It is thus possible to make a statement about the kind of molecules present in an object from a knowledge of its thermoelastic behavior alone.

The straightening out of the chains on stretching leads further to the conclusion that the atoms or groups of atoms belonging to neighboring chains are able to slide over each other like the molecules in a viscous liquid. On the other hand, each atom or group is firmly bound to two neighbors. We can say, therefore, that an atom or group of atoms is in one dimension "solid," *i. e.*, is held by bonds such as occur in a solid body and to which the great internal friction ($> 10^{11}$ poises) of such a body is due. In two other dimensions, however, the atom or group is "liquid," *i. e.*, clings to its neighbors by bonds such as occur in liquids, where the internal friction is less than 10^7 poises. This state of aggregation, which occupies a definite place between the solid and the liquid states, may be conveniently referred to as the rubber-like state.

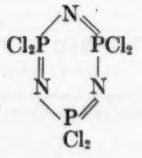
Now the viscosity of rubber amounts to about 10^6 poises; thus it can be compared with the viscosity of a very viscous fluid. As is well known, the viscosity varies enormously with temperature, so a relatively small decrease of temperature makes a very large increase in viscosity and thus transforms rubber into an ordinary amorphous solid. On the other hand, it will be clear that many substances, *e. g.*, polyvinyl acetate, change from a solid into a rubber-like state only above a certain temperature.

Now a decrease of viscosity can be brought about also by addition of a suitable solvent; indeed, many substances built up from chain molecules can be made rubber-like by agents, such as hydrocarbons for rubber, chloroform for polyvinyl acetate, water for gelatine, etc. In these cases one can say that groups of atoms are solid in one direction, and dissolved, *i. e.*, in the liquid state, in two other directions. This special form of the rubber-like state is found in many animal fibers, especially in the contractile elements of muscle.

Probable and Improbable Arrangements

The restoring force thus consists in the chains striving to pass from an improbable arrangement with little possibility of realization (small entropy) to a more probable arrangement with greater possibility of realization (higher entropy). There is only one possible way of realizing the completely stretched form of a primary valency chain, while many crumpled forms are possible. The realizations of non-extended forms are therefore more numerous and their thermodynamic probability is greater.

In order to pass from the stretched to the crumpled state, the chains must be pliable. This conclusion is supported by the following fact. Polyphosphonitrilic chloride and also polymeric sulfur are formed, with absorption of latent heat, from the lower-molecular ring compounds $(NPCl_2)_3$ and S_8. This corresponds to an



increase in entropy on polymerization. From this it follows that atom groups in the polymerized chains have more possibilities of rearrangement, and that the chain elements are more mobile than in the rings.[18]

The transition towards the probable state depends on thermal motion. We can compare the behavior of a stretched rubber chain under the influence of the thermal

blows with the behavior of a rope which is extended in turbulent water: both will show a tension and will contract when the external stress disappears.

The theory of rubber-like elasticity of Meyer, Susich, and Valkó[17] has been extended by Guth and Mark[4] and Kuhn.[8] The latter considers that the most probable form of the chain in the non-stretched condition is a very loose ellipsoidal skein, which is, so to speak, dissolved within a mass formed by the neighboring chains. "The chains thus interpenetrate one another in a complicated manner."

The statistical calculations undertaken by Guth and Mark and by Kuhn showed that in the unoriented state the distance between the two ends of a chain consisting of n members, each of length z, lies between $z\sqrt{n}$ and $z\sqrt[3]{n}$, whereas the chain when stretched out has a length zn.

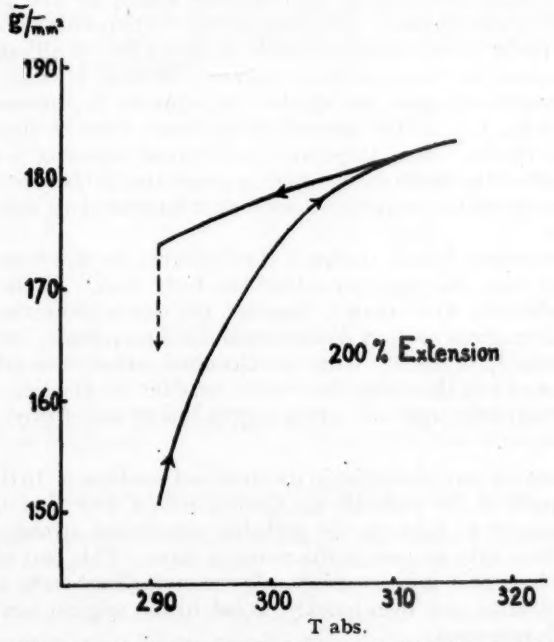


Figure 7—Stress-Temperature Curve of $(NPCl_2)_n$ at 200-Per Cent Extension

The Crystallization of Stretched Rubber Substances

A number of rubber-like substances show, when stretched, crystal interferences; examples are rubber,[7] sulfur,[13,21] polyphosphonitrilic chloride,[15] polyvinyl alcohol.[5] A lattice-like arrangement of zones is thus set up. As has been pointed out, this crystallization can also be detected from the stress-temperature curve.

Now many substances consist of a loose network of chains chemically bound together; to this class belongs, for instance, vulcanized rubber, the chains of which are bound into a network by sulfur bridges, so that individual unattached chains (chemical molecules) practically do not exist, and the whole rubber mass can be considered as one gigantic molecule. In these cases the zones of lattice-like arrange-

ment are smaller in the direction of stretching than corresponds to the length of this giant molecule; only parts of the latter are crystalline, other parts being still amorphous. We consider also that in rubber-like substances containing molecules of finite size crystallization affects only parts of the chains.

Plastic Flow and Relaxation

The internal friction during small deformations of short duration has recently been determined by van der Wyk from the damping of torsional oscillations of slightly stretched rubber threads. At the same temperature, masticated and vulcanized rubber show no appreciable difference. They both have a viscosity of the order of magnitude of 10^6 poises; so here the two materials behave alike. If, on the other hand, we observe the viscosity at large deformations, *e. g.*, the viscosity in plastic flow, we obtain much higher values, and in addition large differences between the different preparations and different values for one preparation at different degrees of deformation. For example, the friction with vulcanized rubber is so large that under a small deforming force no plastic flow at all can be observed.

These phenomena can be explained as follows. Whereas at small deformations only chain elements slip past one another, in a plastic displacement the whole stretched-out chain, *i. e.*, all the elements in the chain, must be displaced relative to the adjacent chains. Here, therefore, the frictional resistance is a direct function of the length of the whole chain, which in masticated rubber has a finite value, whereas vulcanized rubber consists of a network of infinitely long chains chemically bound together.

The shorter the chain length, the less is the friction in the direction of stretching, and the quicker does the stretched rubber-like body relax. In the case of substances with relatively short chains, therefore, the elastic properties can only be observed in deformations of short duration and small magnitude; substances with still shorter chains form fluids. When unvulcanized rubber, or a rubber-like substance, is stretched and the stress observed at constant deformation, a diminution of the stress is normally observed. This may be due to one of two quite different causes:

1. The substance may crystallize in the stretched condition. In the crystallized portions, the parts of the molecule are fixed in such a way that they have no longer the tendency to take up the probable, unoriented arrangement. These portions, therefore, take no part in the restoring force. This part of the stress is also recognizable in that it is reversible. If the crystallized spots are melted by temperature elevation and then quickly cooled to the original temperature, the original stress is recovered.

2. Together with this, however, an irreversible change of stress may be observed, and this is most distinct if the conditions are such that crystallization does not occur. This relaxation must be ascribed to a contraction of the chains due to the slipping of the loosely bound chains over one another. This view has recently been confirmed by Misch and Picken[19] in the case of polyvinyl acetate. In this substance the complication of crystallization does not arise, and the diminution of stress is purely due to slipping. The relaxation is accompanied, as Misch and Picken found, by a diminution in double refraction. Now double refraction is caused by the anisotropic (orientated) arrangement of the chains; a diminution of double refraction indicates therefore a decrease of the degree of orientation. Figures 8 and 9 show that the diminution of double refraction conforms to the relaxation.

Relaxation is also observed with weakly vulcanized rubber; in this case, however, it is limited, *i. e.*, it comes to a standstill after some time, so that the system

is in equilibrium with the tensional force. There we have a substance in which a number of unattached chains are embedded in a network of chains chemically bound together. An unvulcanized system and a vulcanized system are thus intermingled. The elastic and viscous properties are in agreement with this concept.[11] On stretching, both systems are first subjected to stress; the unvulcanized chains, however, are then able to slip past each other, disorientate themselves, and relax, while the net-like system remains in the stressed condition. On removing the external tensile force, the vulcanized system contracts and thereby compresses the relaxed, unvulcanized system, so that an equilibrium is set up between the contracting network and the compressed free chains. These free chains can relieve themselves of the compression by gradual relaxation, so the substance continues to contract very slowly, or creep back, until the original state is regained.

The existence of the netted and of the free chains is also proved by the behavior towards solvents; one part of the weakly vulcanized rubber goes into solution, the other only swells. This division in only two systems is, of course, only a gross representation of the reality; there exist all sorts of transitions from completely free to completely netted chains.

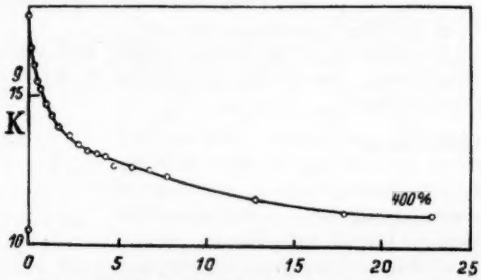


Figure 8—Rate of Relaxation of Stretched Polyvinyl Acetate at 400-Per Cent Elongation and 70°. Abscissa: Time in Minutes

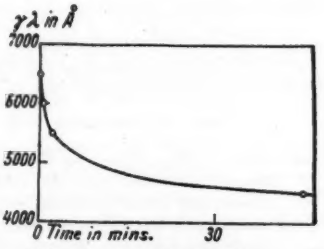


Figure 9—Diminution of Double-Refraction during Relaxation of Polyvinyl Acetate at 400-Per Cent Elongation and 70°

Biological Systems in the Rubber-like State

It has already been stated that a number of substances, chemically quite different, can occur in the rubber-like state. It appears to us to be of a special interest that this state of aggregation is of widespread occurrence in nature. No one would, for example, designate the state of aggregation of our muscles as liquid; however, they are certainly not solid, as physiologists quote the observation that microscopic worms can perforate the muscle fibrillae and slip through without leaving any hole or other damage subsequently visible. Also the viscosity, determined by the damping of a tuning fork, corresponds with that of a very viscous liquid.[3]

Now the stress-temperature curve of the non-excitated passively stretched muscle shows that it is in the rubber-like state.[17] The muscle possesses, therefore, main valency chains which pass from end to end and which, in the resting muscle, are not fully extended. They are connected with neighboring chains, like the corresponding chains in amorphous rubber, only by liquid bonds which thus determine the mechanical consistency.

By passive extension they are stretched, and the contraction of the passively extended muscle is due to the tendency to pass from this orientated and improbable into the more probable original state. The observations, however, take us further. The stress-temperature curve of the passively-stretched muscle shows

that on extension a certain crystallization takes place, and this is confirmed by x-ray examination. The active contraction, however, is of quite another nature. The contracted muscle behaves as a normal solid substance: the liquid linkages are converted into solid linkages, which can only be ascribed to a chemical change.

Now, the rubber-like properties of muscle are intimately connected with its water content; so we may suppose that the two-dimensional liquid state of the main valency chains of the contractile elements is based on the fact that the chains are surrounded by water. In the contracted state, however, they behave as a solid; so we can say that the uncontracted dissolved protein chains become insoluble, coagulated, on active contraction.

Passively-stretched muscle relaxes to a limited extent, this relaxation being accompanied by a diminution in double refraction. From this we may conclude that in muscle, as in weakly vulcanized rubber, a netted system is present along with an unnetted system. It appears that the relative proportions of the two types of system are different in different kinds of muscle. For example, the smooth muscles of the invertebrates have a very pronounced unnetted component, with marked relaxation, while the transversely-striped muscles relax much less.

The elastic fibers *e. g.*, those of the arterial system, form also a netted rubber-like system; the same is the case with the membrane of the blood corpuscles, and many other biological systems could be added to the list.

It thus appears that the study of the physical properties of rubber and their explanation in terms of molecular mechanics has led to conclusions of a more general nature than has been hitherto suspected.

References

[1] Busse, *J. Phys. Chem.*, **34**, 2870 (1932).
[2] Ferri, *Helv. Chim. Acta.*, **20**, 1393 (1937).
[3] Gasser and Hill, *Proc. Royal Soc.*, (B) **96**, 398 (1924).
[4] Guth and Mark, *Monatsh.*, **65**, 93 (1934).
[5] Halle and Hoffmann, *Naturw.*, **23**, 770 (1935).
[6] Karrer, *Phys. Rev.*, **39**, 857 (1932).
[7] Katz, *Naturw.*, **13**, 411 (1925).
[8] Kuhn, *Kolloid-Z.*, **76**, 258 (1936).
[9] Lotmar and Meyer, *Monatsh.*, **69**, 115 (1936).
[10] Mark and Susich, *Kolloid-Z.*, **46**, 11 (1929).
[11] Meyer and Ferri, *Helv. Chim. Acta.*, **18**, 570 (1935); **19**, 694 (1936); *Pflügers Archiv.*, **238**, 78 (1936).
[12] Meyer and Hohenemser, *Helv. Chim. Acta.*, **18**, 1061 (1935).
[13] Meyer and Go, *Helv. Chim. Acta.*, **17**, 1081 (1934).
[14] Meyer and Mark, *Ber.*, **61**, 1928 (1928); "Der Aufbau der Hochpolymeren," **1930**.
[15] Meyer and Pankow, *Helv. Chim. Acta.*, **19**, 930 (1936).
[16] Meyer and Picken, *Proc. Royal Soc.*, (B) **124**, 29 (1937).
[17] Meyer, Valkó, and Susich, *Kolloid-Z.*, **59**, 208 (1932).
[18] Meyer, *Trans. Faraday Soc.*, **32**, 148 (1935).
[19] Misch and Picken, *Z. physik. Chem.*, (B) **36**, 398 (1937).
[20] Stokes, *Am. Chem. J.*, **17**, 275 (1895).
[21] Trillat and Forestier, *Bull. Soc. Chim.*, Paris (4), **51**, 248 (1932).
[22] Weber, "The Chemistry of India Rubber," London. **1902**; *Ber.*, **33**, 785 (1900).

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Chemical Structure of Vulcanized Rubber

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A CENTURY ago, Charles Goodyear in America and Th. Hancock in England found that the properties of crude rubber could be greatly improved by heating it with sulfur. The product resulting was more elastic, more resistant to tear and abrasion, less affected by solvents, and decidedly less thermoplastic. The treatment of rubber to give these desired properties is known generally as vulcanization and must be considered as the basis for the enormous growth of the rubber industry and the extensive use of rubber products in our everyday life.

Broadly speaking, vulcanization involves the reaction, in some fashion, of sulfur with rubber. Extensive investigation has revealed other substances, such as benzoyl peroxide or polynitrobenzenes, which can transform rubber into a "vulcanized" condition. Experience has also shown that metallic salts of zinc or lead and especially certain organic compounds called "accelerators" greatly affect the rate of vulcanization, and these are favorably employed in practice. A vast amount of empirical knowledge has been gained which has greatly improved the practical application of vulcanization and the quality of rubber products, but which has failed as yet to reveal a complete picture of the true nature of the process.

However, the past century has not been without many serious attempts to postulate tenable theories which would help to explain vulcanization. As our knowledge of rubber has increased, so have the angles of attack upon the problem been enlarged, and new points of view have been included. The very complexity of the reaction, as well as our incomplete knowledge of rubber itself, probably precludes any simple and immediate solution to the difficulty, but further investigation into some of the more obscure phases of the process ought to add greatly to our understanding.

Most theories of vulcanization attempt to explain how sulfur can react to build up a stable structure after the disaggregating action of milling and heat (oxidation) has reduced the rubber to a plastic state. It is evident that sulfur does combine chemically with the rubber. Some ultracolloidally minded investigators have based the change in properties upon the reinforcing action of a rubber sulfide product dispersed in the rubber matrix (*20*, *22*); others have based it upon the change in aggregation of the combined prod-

uct under the influence of accelerators and zinc salts (*27*). From the chemical point of view, some have suggested polymerization of the rubber molecules under the catalytic influence of sulfur with combination of sulfur as incidental (*21*, *24*); others have postulated the formation of definite sulfur bonds or linkages which tie the chainlike rubber units together into a structure capable of explaining the vast change in properties (*17*, *23*). Combinations of two or more of these possibilities have also been suggested (*16*), and each has its own line of experimental evidence upon which the theory is based.

While the chemical combination of sulfur with rubber may be either directly responsible for vulcanization or only incidental to other more important changes, it is nevertheless significant enough to consider what influence it may have in the total transformation taking place.

THE physical properties of a vulcanizate do not depend upon the proportion of combined sulfur when different mixtures are considered. The effect of accelerators will greatly influence the combination of sulfur and the resulting state of the compound. However, for any given mixture and conditions of vulcanization, the combined sulfur and physical properties have a close relation. If a rubber-sulfur compound is thus thought to be responsible for building up the vulcanized state, the additional fact of reversion under continued cure must be considered. This softening effect of heat on the vulcanized rubber appears to be quite distinct and different from the effect of heat on crude rubber. The possibility that this is due to changes in the chemical combination of rubber and sulfur or to other physical changes in the vulcanized state has never been determined.[1]

In order to explain the formation of a vulcanized structure by widely different amounts of combined sulfur, depending on the type of acceleration used, it would seem plausible to suggest that sulfur combines in different ways with the rubber. The formation of soft and hard vulcanized rubber (ebonite) has been discussed as two separate reactions of sulfur with rubber, one in which the sulfur reacts with the terminal unsaturation on the ends of the rubber molecule to produce soft rubber, and the other where sulfur adds to internal double bonds to give ebonite (*2*). Other types of combination have been proposed (*4*, *11*, *13*), but almost no direct experimental evidence exists as to whether the sulfur combines as a sulfide, disulfide, thioözonide, or sulfhydryl group. Also, it is uncertain as to whether the sulfur com-

[1] In a recent paper, Garvey and Forman showed that accelerators in low-sulfur compounds fall into two groups, producing either reverting or nonreverting stocks [IND. ENG. CHEM., **30**, 1036 (1938)]. They suggested that the vulcanized state may depend on the maintenance of an adequate number of cross bonds by a dynamic equilibrium between accelerator action and heat reversion, rather than on the permanence of individual cross bonds.

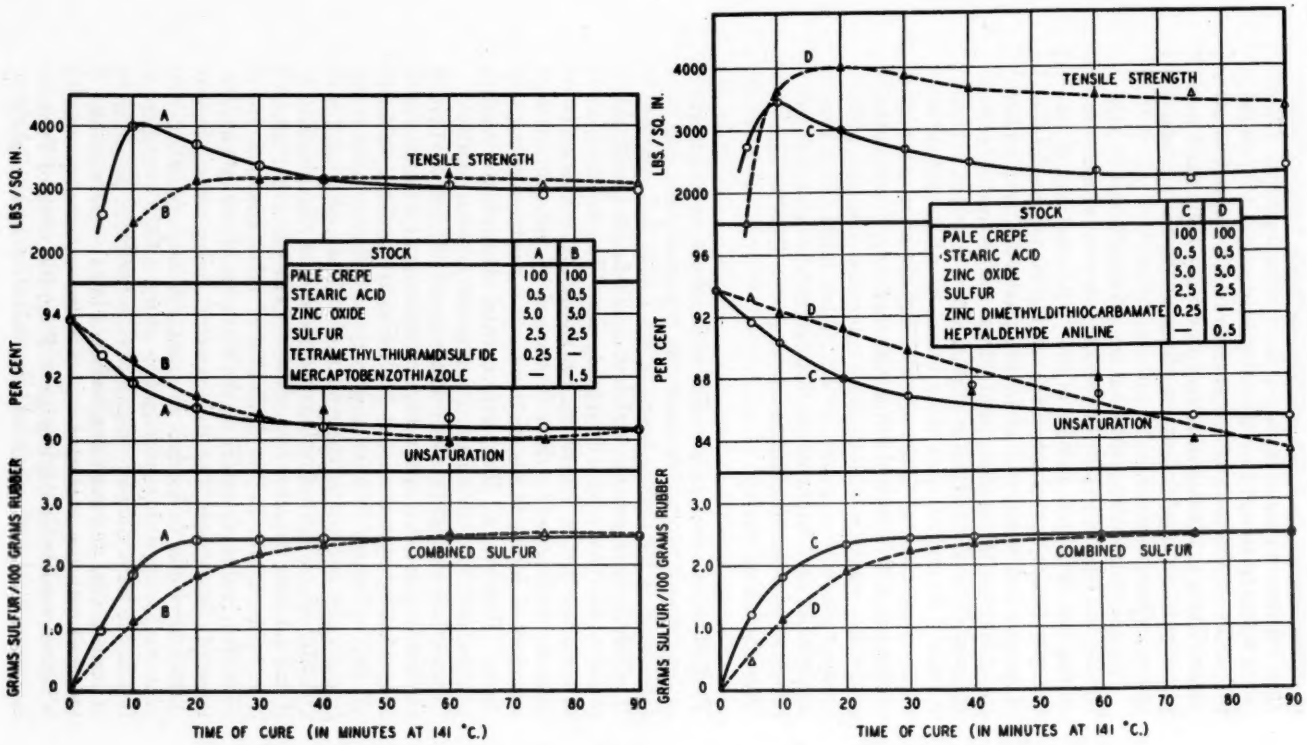
TENSILE STRENGTH
UNSATURATION
COMBINED SULFUR
LBS. / SQ. IN.
PER CENT
GRAMS SULFUR / 100 GRAMS RUBBER
TIME OF CURE (IN MINUTES AT 141 °C.)
STOCK | A | B
PALE CREPE | 100 | 100
STEARIC ACID | 0.5 | 0.5
ZINC OXIDE | 5.0 | 5.0
SULFUR | 2.5 | 2.5
TETRAMETHYLTHIURAMDISULFIDE | 0.25 | —
MERCAPTOBENZOTHIAZOLE | — | 1.5
STOCK | C | D
PALE CREPE | 100 | 100
STEARIC ACID | 0.5 | 0.5
ZINC OXIDE | 5.0 | 5.0
SULFUR | 2.5 | 2.5
ZINC DIMETHYLDITHIOCARBAMATE | 0.25 | —
HEPTALDEHYDE ANILINE | — | 0.5

FIGURE 1. PHYSICAL AND CHEMICAL PROPERTIES *vs.* TIME OF CURE FOR STOCKS *A* TO *D*

bination is intramolecular, as in the union with terminal groups or internal double bonds, either adjacent or separated, or intermolecular, as in the formation of sulfur bonds or linkages between separate rubber units or chain groups. The latter would be thought to be most closely related to physical properties on the basis of the structure built up, but in all probability a combination of the two usually occurs and the inability to distinguish between them has so far prevented any experimental proof.

The ability of sulfur, or sulfur compounds, to act in this fashion has been shown in the case of other substances possessing double bonds, such as in the "vulcanization" of certain oils (factice-rubber substitute) and in the polymerization of acrylic resins, as well as in the production of Thiokol (polyethylene tetrasulfide) and other sulfur-bearing compounds. The effect of sulfur in producing vulcanized rubber is largely dependent upon the presence of either natural or added accelerators. These are thought either to react to produce an active type of sulfur which will combine with the rubber in a particular way to give a vulcanized structure, or to create more active groups in the rubber itself. But here again it has been impossible to distinguish between these two effects or to determine what particular type of sulfur combination is taking place.

THE chemical reaction of sulfur with rubber, or polymerization between two rubber molecules, is generally assumed to take place at the double bonds of the rubber hydrocarbon. If rubber is hydrogenated with loss of the double bonds, the ability to be vulcanized is completely lost. The development of synthetic rubber substitutes has shown that a state analogous to "vulcanized" rubber is reached by polymerization with loss of double bonds, as in certain derivatives of butadiene. However, all direct experimental attempts to reveal polymerization in vulcanized rubber have so far been negative. Considerable evidence has been accumulated which shows that the loss in unsaturation of rubber on vulcanization is directly accounted for by the amount of chemically combined sulfur (*8*, *18*). Changes in specific gravity and the index of refraction also indicate a linear relation with combined sulfur (*10*, *26*). If polymerization has occurred during vulcanization, it has not been detected by methods of analysis so far used.

In connection with the discussion of polymerization, recent work in this laboratory on the heat-pressure treatment of latex (*5*) has shown that it is possible under certain conditions to obtain an increase in unsaturation of about 2 per cent, suggesting a depolymerization of the rubber hydrocarbon in the latex globule. (Since the electrokinetic potential of heat-treated and even deproteinized latex is more or less identical with the untreated material, the adsorbed protein is not responsible for this change.) From the work of Pummerer and Stärk (*15*), who found that sol rubber had a slightly

higher unsaturation value than gel rubber, it may be inferred that a transition from the gel to the sol state has occurred in the outer layer of the latex particle. This is further manifest by the change in shape of the particles from pearlike to spherical, and the ease of obtaining complete solution of the dried rubber in benzene without previous mastication. That the rubber hydrocarbon is more homogeneous after heat treatment or depolymerization is also evident from its more uniform physical properties when vulcanized and its increased rate of combination with sulfur, as compared with rubber obtained directly from normal unheated latex.

IN VIEW of the fact that sulfur may be combining in different ways with rubber, especially under the influence of accelerators, it would be interesting to study the possible types of sulfur combination and the corresponding change in unsaturation of the rubber hydrocarbon. Most of the existing data on the change in unsaturation with combined sulfur has been based on simple rubber-sulfur vulcanizates where it has been found that the loss of one double bond is equivalent to the addition of one atom of chemically combined sulfur. This would point to one fixed type of sulfur combination which does not have any direct relation with the structure of the vulcanized rubber as revealed by its physical properties. If sulfur is important in building up a structure by means of intermolecular bridges, such chemically combined sulfur ought to bear some relation to the physical properties. Likewise, the change in unsaturation of the rubber hydrocarbon ought to reveal in what manner the sulfur combination occurs. Since changes in physical properties are most marked when accelerators are used, a series of typical low-sulfur, highly accelerated compounds were first studied in an attempt to throw some light on the type of sulfur combination.

The unsaturation was measured by the iodine chloride absorption method of Kemp (*7*, *8*, *9*) as modified by Blake and Bruce (*1*), using *p*-dichlorobenzene as a solvent. Combined sulfur was determined as the difference between total sulfur and free sulfur as measured by sodium sulfite extraction (*14*). This was also checked by determining combined sulfur directly on the acetone-extracted residue. The results of the measurements along with the physical properties of the four vulcanized stocks, which differ only in the accelerator used, are summarized in Table I. These data are plotted against the time of cure in Figure 1. In order to show the relation between the change in unsaturation and the amount of sulfur combining during a given cure, the data in the two parts of Figure 1 were replotted against each other in Figure 2. The straight lines indicate the theoretical relations resulting when sulfur is combining either as one or two atoms per double bond. The calculations consider the unsaturation of crude rubber as one double bond for every C_5H_8 unit;

all data are calculated on the basis of the crude rubber in the compound.

As expected, the combined sulfur bears no direct relation to the physical properties of the vulcanized stocks. For example, the rate of combination of sulfur in stocks *A* and *C* is almost exactly the same, yet the tensile strength of *C* is considerably lower than that of *A*. The same is true of *B* and *D*. The change in unsaturation also shows no cor-

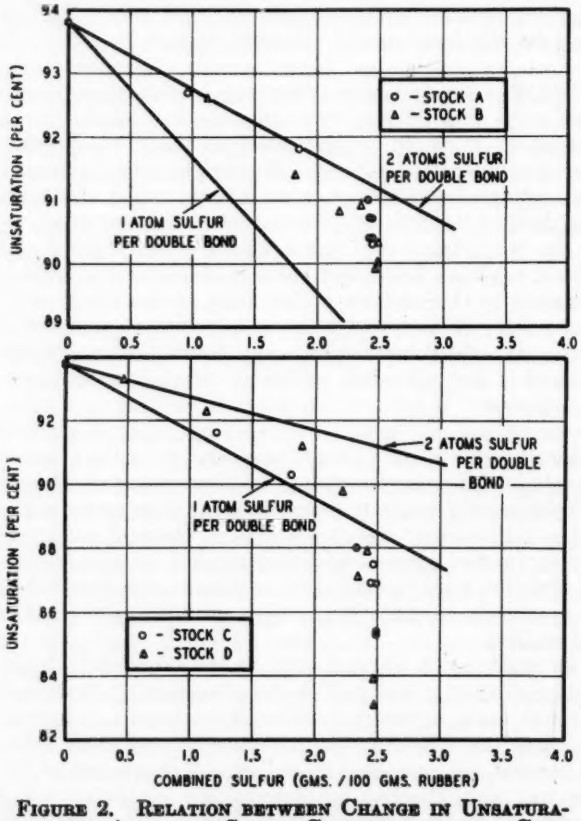

FIGURE 2. RELATION BETWEEN CHANGE IN UNSATURATION AND AMOUNT OF SULFUR COMBINING DURING A CURE FOR STOCKS *A* TO *D*

relation with physical tests; yet when the combined sulfur is compared with the loss in double bonds, an interesting point is revealed. In stocks *A*, *B*, and *D*, the sulfur is evidently combining in excess of the customarily thought relation of one atom of sulfur saturating one double bond, as seems to be the case in stock *C*. The relation is practically linear while most of the sulfur is combining, but after the optimum cure has been reached and most of the sulfur is combined, the values for unsaturation decrease rapidly, es-

pecially in stocks *C* and *D*. This fact is undoubtedly connected with the problem of reversion and the loss in resistance to heat and aging. It is not safe to say, however, that these low values of unsaturation represent the exact state of the vulcanized compound. More likely, a loss in double bonds has occurred during the dispersion of the

TABLE I. SUMMARY OF DATA ON ACCELERATED, LOW-SULFUR STOCKS

Stock	Time of Cure at 141° C.	Combined Sulfur per 100 G. Rubber	Unsaturation	Tensile Strength	Modulus at 500%	Elongation at Break
	Min.	*Grams*	%	*Lb. per sq. in.*		%
A	0	0.00	93.8	...	...	...
	5	0.96	92.7	2580	245	900
	10	1.85	91.8	4000	455	835
	20	2.40	91.0	3710	390	870
	30	2.42	90.7	3370	330	915
	40	2.42	90.4	3140	285	925
	60	2.43	90.7	3060	280	935
	75	2.43	90.4	2900	270	955
	90	2.44	90.3	2960	270	965
B	0	0.00	93.8	...	...	...
	10	1.12	92.6	2435	260	900
	20	1.82	91.4	3110	310	895
	30	2.18	90.8	3140	350	910
	40	2.35	90.9	3145	315	910
	60	2.47	89.9	3230	305	930
	75	2.48	90.0	3060	285	935
	90	2.48	90.3	3070	275	955
C	0	0.00	93.8	...	...	...
	5	1.21	91.6	2740	280	885
	10	1.81	90.3	3470	385	850
	20	2.33	88.0	3000	350	860
	30	2.45	86.9	2700	305	875
	40	2.47	87.5	2500	280	900
	60	2.48	86.9	2320	255	900
	75	2.48	85.4	2180	245	935
	90	2.47	85.3	2400	240	945
D	0	0.00	93.8	...	...	...
	5	0.47	93.3	1500	130	980
	10	1.13	92.3	3640	430	825
	20	1.90	91.2	4000	1000	705
	30	2.22	89.8	3880	1060	690
	40	2.35	87.1	3680	985	680
	60	2.42	87.9	3560	870	670
	75	2.47	83.9	3530	625	690
	90	2.48	83.1	3320	670	700

sample in the heated solvent, possibly through cyclization or addition of oxygen. However, some difference must exist in the stability of the double bonds in the overcured compounds since all samples were treated in exactly the same manner in testing for unsaturation.

IN ORDER to compare the effect of accelerators and zinc oxide in the previous compounds, two more stocks were tested in the same manner. One contained only rubber and sulfur and the other rubber, sulfur, and zinc oxide. The results are summarized in Table II and plotted as before in Figures 3 and 4 (stocks *E* and *F*).

The simple rubber-sulfur compound *E* shows the well-established relation of one sulfur atom saturating one double bond and verifies the experimental procedure with previous work. The effect of adding zinc oxide is shown in earlier parts of the cure with stock *F*. The improved tensile strength and modulus are accompanied by an actual decrease in the rate of combination of sulfur, yet the relation of combined sulfur to unsaturation in this case appears more like that observed in the accelerated compounds which showed good tensile and modulus properties. The effect of overcure is again apparent in the extremely low unsaturation value of 64.2 per cent obtained for *E* after 10-hour cure, where normally the linear relation of one atom of sulfur per double bond would give a value of 78.7 per cent at 7.43 grams combined sulfur.

TABLE II. SUMMARY OF DATA ON RUBBER-SULFUR AND RUBBER-SULFUR-ZINC OXIDE STOCKS

Stock	Time of Cure at 141° C.	Combined Sulfur per 100 G. Rubber	Unsaturation	Tensile Strength	Modulus at 500%	Elongation at Break
	Hr.	*Grams*	%	*Lb. per sq. in.*		%
E	0	0.00	94.5	...	...	...
	2	1.77	90.9	960	110	980
	3	2.73	88.7	1970	150	985
	4	3.63	86.9	3210	230	980
	6	5.46	82.9	3160	435	810
	10	7.43	64.2	450	...	430
F	0	0.00	94.5	...	...	...
	0.5	0.31	94.0	535	55	1060
	1	0.64	93.7	1060	100	985
	1.5	1.03	93.2	1660	115	985
	2	1.45	92.5	1765	145	940
	2.5	1.69	92.4	2110	170	935
	3	2.10	91.1	2380	210	915

The combination of sulfur in excess of one atom of sulfur for each double bond saturated may be due to different types of combination with or without the double bonds in the rubber hydrocarbon, or possibly with the nonrubber constitutents in the compounds. The latter substances do not affect the measurement of unsaturation, according to Kemp, but conceivably some sulfur might be combined in the unextractable material as zinc sulfide or with resins and proteins. As a result of the practically linear relation between unsaturation and combined sulfur until overcure begins, this effect must be small and not significant within the experimental accuracy of the data. Treatment of the four accelerated compounds was identical in every respect, so that any difference must be based on the accelerator used. Reactions of sulfur with substances other than the rubber would hardly account for the change in type of sulfur combination between stocks *A* and *C*. Kelly (*6*) investigated the combination of sulfur with nonrubber constitutents in stocks containing zinc oxide and certain accelerators and found it to be appreciable, but his stocks contained twice as much sulfur

and three to five times as much zinc oxide as were employed in the present investigation. Although this possibility cannot be entirely dismissed, it is felt that it does not detract from the value of the results obtained.

The possible types of combination of sulfur with rubber which would cause the above results are merely speculative (Figure 5). Conceivably a disulfide might exist, but it would hardly be thought to be stable enough to remain as such or to

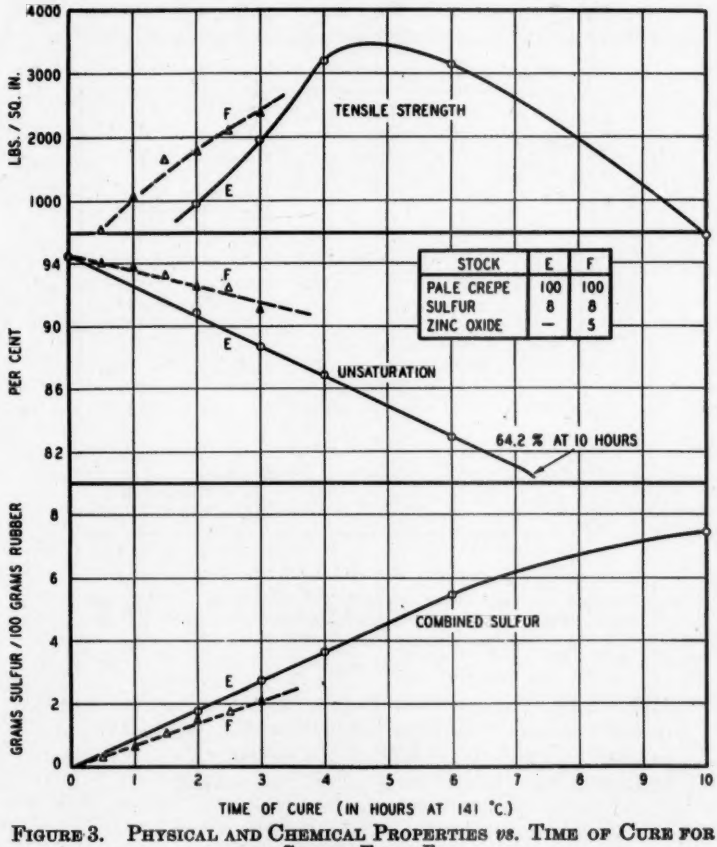

FIGURE 3. PHYSICAL AND CHEMICAL PROPERTIES *vs.* TIME OF CURE FOR STOCKS *E* AND *F*

be as strong a linkage as a single sulfur bridge. Thiozone might form which could add three sulfur atoms per double bond in forming an ozonide type addition. Undoubtedly some combination of several different reactions could explain it. Sulfur could dehydrogenate the rubber hydrocarbon next to the double bond with formation of hydrogen sulfide and form an intermolecular sulfur bridge without loss of unsaturation. This type of reaction, accompanied by direct addition of sulfur at the double bond or sulfur bridging

between double bonds, could produce a vulcanized structure without losing a double bond for every sulfur atom chemically combined.

Direct experimental proof of such sulfur combinations does not exist, although it is known that in certain cases hydrogen sulfide is evolved during vulcanization and sometimes continues to be evolved from vulcanized rubber, especially when heated (*21*, *28*). Hard rubber containing over 32 per cent combined sulfur must be the result of some substitution of sulfur in the rubber hydrocarbon in excess of that required for complete saturation of the double bonds.

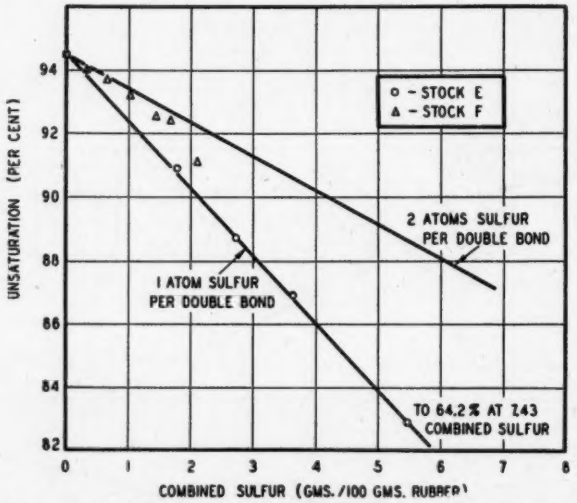

FIGURE 4. RELATION BETWEEN CHANGE IN UNSATURATION AND AMOUNT OF SULFUR COMBINING DURING A CURE FOR STOCKS *E* AND *F*

RECENTLY, Meyer and Hohenemser (*12*) proposed the use of methyl iodide in testing for thioether linkages in vulcanized rubber. Alkyl halides are known to add to alkyl sulfides or thioethers to form sulfonium compounds:

$$R{-}S{-}R + CH_3I \longrightarrow \begin{matrix} R & R \\ & S \\ CH_3 & I \end{matrix}$$

By treating vulcanized rubber with an excess of methyl iodide and measuring the iodine combined after reaction for 2 days at room temperature, they found that part of the sulfur had combined in the form of thioether linkages. If this reaction is a specific test for that type of sulfur combination, it would be an excellent way of determining whether a vulcanized structure could be built up by such sulfur bridges.

The Meyer and Hohenemser test was applied to the previous series of accelerated and nonaccelerated compounds. According to their procedure, values of thioether sulfur accounted for 20 to 60 per cent of the total combined sulfur at any given time of cure. These values varied according to the accelerators used, and the accelerator producing the highest tensile and modulus had the lowest amount of thioether sulfur. Also the rate of thioether combination was roughly proportional to the rate of total sulfur combination, showing no definite correlation with physical tests and no decrease in thioether linkages during overcure.

Either thioether linkages have no relation to physical properties, or else the basic assumptions of the test are not justified. Some experimentation has already shown that the value of thioether sulfur will vary considerably with the

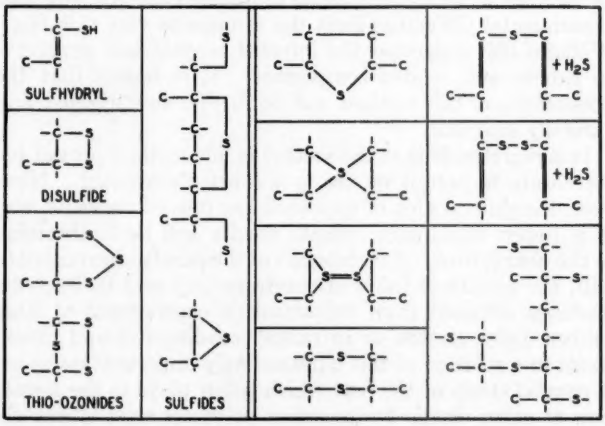

FIGURE 5. POSSIBLE TYPES OF SULFUR COMBINATIONS IN VULCANIZED RUBBER

time of reaction of the methyl iodide and the acetone-extracted vulcanized rubber. This would indicate that the reaction may not be completed within 2 days for some compounds. Two days of reaction time were found to be sufficient to check the amount of sulfur in certain thioether compounds physically added to unvulcanized rubber, but with certain vulcanizates the values of thioether sulfur varied in such a manner that side reactions and possible decomposition effects were strongly suspected. Likewise, the literature reveals that methyl iodide is also capable of forming addition compounds containing one or more iodine atoms with such substances as ethylene sulfide (*3*) and organic disulfides (*19*). Since the possibility of such types of sulfur combinations cannot be excluded from vulcanized rubber, it is extremely doubtful that the methyl iodide test is suffi-

ciently reliable for the study of sulfur linkages produced in vulcanization.

ATTEMPTS are being made to apply other tests to vulcanized rubber in an effort to determine what types of sulfur combination take place under different conditions of vulcanization and what bearing they may have on the physical structure built up. Some preliminary experiments have indicated that the mercaptan or sulfhydryl group is probably not present, at least after the sample has been dispersed by heating in a solvent. The application of chemical tests is rather handicapped by the necessity of either dispersing the sample in a solvent or else finding reactions which can be applied to the solid rubber. For a true picture of the vulcanized structure it should be studied without any possible interference from solvents or chemical reagents. Such an approach could be secured by studying Raman or infrared spectra, although experimental difficulties limit the samples to very thin films. Williams (*25*) suggested the infrared technic and applied it to rubber and related compounds. It is hoped that the possibilities of this method will be further investigated and carefully analyzed.

It is regrettable that the methyl iodide method proved too inaccurate to permit its use to the extent expected. However, the general idea of approach has proved its value, and it is hoped that more definite results will be forthcoming in the near future. A correlation of the purely chemical data with the results of infrared spectrography and indirect deductions obtained from vulcanization experiments of latex rubber under stretch or in racked condition should finally result in a solution of this outstandingly important question. A parallel study of the part which sulfur plays in the formation of other elastic hydrocarbon polymers must ultimately permit us to draw basic conclusions concerning a general rule to control these reactions.

Acknowledgment

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Literature Cited

(1) Blake, J. T., and Bruce, P. L., *Ind. Eng. Chem.*, 29, 866 (1937).
(2) Boggs, C. R., and Blake, J. T., *Ibid.*, 22, 748 (1930).
(3) Delépine, M., *Compt. rend.*, 171, 36 (1920).
(4) Garvey, B. S., Jr., and Thompson, G., *Ind. Eng. Chem.*, 25, 1292 (1933).
(5) Jordan, W. F., M.S. thesis, Mass. Inst. Tech., 1936.
(6) Kelly, W. J., *J. Ind. Eng. Chem.*, 12, 875 (1920).
(7) Kemp, A. R., *Ibid.*, 19, 531 (1927).
(8) Kemp, A. R., Bishop, W. S., and Lackner, T. J., *Ibid.*, 20, 427 (1928).
(9) Kemp, A. R., and Mueller, G. S., *Ind. Eng. Chem., Anal. Ed.*, 6, 52 (1934).

(10) Kirchhof, F., *Kautschuk*, **9**, 172 (1933).
(11) Kirchhof, F., *Kolloid.-Z.*, **13**, 49 (1913); **14**, 35 (1914).
(12) Meyer, K. H., and Hohenemser, W., *Helv. Chim. Acta*, **18**, 1061 (1935).
(13) Midgley, T., Henne, A. L., Shepard, A. F., and Renoll, M., *J. Am. Chem. Soc.*, **56**, 1325 (1934).
(14) Oldham, E. W., Baker, L. M., and Craytor, M. W., *Ind. Eng. Chem., Anal. Ed.*, **8**, 41 (1936).
(15) Pummerer, R., and Stärk, H., *Ber.*, **64**, 825 (1931).
(16) Rossem, A. van, *India Rubber J.*, **92**, 845 (1936).
(17) Rossem, A. van, and Dekker, P., *Kautschuk*, **7**, 202 (1931).
(18) Spence, D., and Scott, J. H., *Kolloid.-Z.*, **8**, 304 (1911).
(19) Steinkopf, W., and Muller, S., *Ber.*, 56B, 301 (1926).
(20) Stevens, H. P., *J. Soc. Chem. Ind.*, **47**, 37T (1928).
(21) Stevens, H. P., and Stevens, W. H., *Ibid.*, **51**, 44T (1932).
(22) Twiss, D. F., *Trans. Inst. Rubber Ind.*, **9**, 275 (1933).
(23) Weber, C. O., "Chemistry of India Rubber," 1902.
(24) Whitby, G. S., *Trans. Inst. Rubber Ind.*, **6**, 61 (1930).
(25) Williams, D., *Physics*, **7**, 399 (1936).
(26) Williams, I., *Ind. Eng. Chem.*, **26**, 746 (1934).
(27) *Ibid.*, **26**, 1190 (1934).
(28) Wolesensky, E., *Bur. Standards J. Research*, **4**, 501 (1930).

[Translated by Wm. C. Bleher for Rubber Chemistry and Technology from the Sitzungsberichte der Akademie der Wissenschaften in Wien, Mathematisch-Naturwissenschaftliche Klasse, Abteilung IIb Chemie, Vol. 146, No. 10, pages 755–762, 792–796, 1938.]

The Statistical Theory of the Elasticity of Rubber

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Introduction

The theoretical investigations of various authors,[1] with the aid of which the physical properties of rubber-like substances have become understood on a basis of intermolecular statistics, have not, at least from a quantitative point of view, kept pace with investigations relating to kinetic theories of gases. However, only the facts of rubber elasticity have become understood, and to point out one case, the coefficient of elasticity cannot be derived, and much less the tension zone, beyond proportionality. The reason for this is that, although statistics of a single chain molecule of finite size can be compiled, the bond of the chain molecule and, as a further instance, the behavior of a molecule of infinite size formed by interlacing have not been clearly understood up to the present time. Consequently, it has been possible to gain an insight into the statistical behavior of individual chain molecules much more easily than into that of a piece of rubber, and therefore to deduce with less difficulty theories of the viscosity of high molecular solutions and similar systems. In the case of rubber, progress has been more difficult in explaining the effects which take place.

The present status of the theory of rubber is explained in a work of Kuhn,[2] where the attempt is made to explain the experimental elasticity data quantitatively. His calculation gives a coefficient of elasticity approximately equal to:

$$\epsilon = 7G_0kT \qquad (1)$$

in which G_0 represents the number of chain molecules per unit volume (the correction factor 7 is to take care of small variations). It is evident at once, however, that this has a limited value. Any completely vulcanized piece of rubber can be regarded as one large molecule, in which case according to Equation 1 it would necessarily have very little elasticity. Consequently, Equation 1 is applicable only with the assumption of unramified chains. However, in spite of this reservation the relation between ϵ and the size of the molecule, based on Equation 1, would be contrary to what would be expected experimentally, for according to Equation 1 the coefficient of elasticity increases by subdivision of the molecule. Within the range of low degrees of vulcanization which still correspond to finite molecules of mean size, experiment shows the opposite to be true.

The Introduction of Viscosity in the Theory of Rubber

The contradiction pointed out above gives a starting point for finding a correct method. The following two requirements may be established, both of which are naturally abstract:

1. The number of molecules per unit volume (G_0) shall not appear explicitly in the equation. With this the following postulate is very closely connected.
2. A subdivision or multiplication of the mean chain length shall have practically no influence on the behavior observed. It is clear that the first rule cannot

be satisfied readily, because by calculating the determinant physical quantity, namely, the entropy per unit volume, all the molecules of the unit volume must be included, in which G_0 must appear in some form.

The juxtaposition of a crystal phase and a so-called fused state leads to the idea in the second phase of this report, which alone is of interest, that viscosity is effective at small distances in spite of the fact that the fused state does not from a macroscopic point of view appear to be liquid. This viscosity, however, hinders the relative movements of adjacent parts of the chain molecules, and therefore the total extension of any chain molecule is of no significance in a first approximation of the physical behavior, assuming that the chain length is not too small for plasticity still to exist. In particular, with increase in the density of the places of interlacing, the point at which the mean size of the molecules changes from finite values to infinite values will in no way be evident. The part played by viscosity can be made particularly clear by comparing Buna rubber with natural rubber. In the original state (dried solution), notwithstanding the practically equal size of the molecules, Buna is plastic, whereas natural rubber is elastic. The two chemical formulas show that the probability of interlaced points being formed in both cases is about the same, since the double bond of rubber is only slightly less reactive than the double bond of Buna. The difference in the physical behavior must be explained by the viscosity effect, since adjacent rubber chains, due to the methyl substitutions, are in a much poorer position to slide by one another than are adjacent Buna chains—an evident case of friction.

The Principle of Calculating the Elasticity of Rubber

For the quantitative application of the concepts described above, it is necessary to depend on the method already utilized. According to this, the stress is calculated by the expression:

$$s = \frac{dF}{d\lambda} \tag{2}$$

for an elongation of $(1 + \lambda):1$, where F represents the free energy per unit volume. As is well known:

$$F = U - TS \tag{3}$$

where the internal energy U as well as the entropy S must likewise be taken per unit volume. In the following equation, deduced from (3):

$$S = \frac{dU}{d\lambda} - T\frac{dS}{d\lambda}$$

the subtrahend can at a perfect entropy elasticity be neglected, so that:

$$s = -T\frac{dS}{d\lambda} \tag{4}$$

The problem is to express S for the various states of elongation. According to Kuhn, the value of S is as follows:

$$S = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} G_0\left(c_1 - k\frac{x^2 + y^2 + z^2}{2b^2Z}\right) e^{-\frac{(x^2+y^2)(1-\lambda)+z^2/(1+\lambda)^2}{2b^2Z}}\left(\frac{1}{b\sqrt{2\pi Z}}\right)^3 dxdydz \tag{5}$$

This equation is based on the fact that the individual entropy:

$$\left(c_1 - k\frac{x^2 + y^2 + z^2}{2b^2Z}\right)$$

which is derived from the intermolecular statistics of the single, unstressed chain is integrated for all conceivable dimensions (x, y, z), whereby the molecular number G_0 as well as the weight factor:

$$e^{-\frac{(x^2+y^2)(1-\lambda)+z^2/(1+\lambda)^2}{2b^2Z}}\left(\frac{1}{b\sqrt{2\pi Z}}\right)^3 dxdydz$$

appears as factors in the equation. Z represents the chain member number, $b = \frac{l_0}{\sqrt{3}}\cot\frac{\alpha}{2}$ with the length of the chain member l_0 and valence angle $\pi-\alpha$. c_1 represents a standardization constant. The weight function is the probability that the length falls within the intervals of:

$$x_1, x_1 + dx_1;\ y_1, y_1 + dy_1;\ z_1, z_1 + dz_1$$

where $x_1;\ y_1;\ z_1$ are related to $x;\ y;\ z$ as follows:

$$x_1 = x\sqrt{1-\lambda};\ y_1 = y\sqrt{1-\lambda};\ z_1 = \frac{z}{1+\lambda} \qquad (6)$$

The transformation relations (6) correspond to the change in length resulting from linear extension at constant volume. Due to the deformation, the weight function, which has been modified in (6), must be introduced in Equation 5. From Equation 5 we obtain, by means of Equation 4, for the coefficient of elasticity:

$$\epsilon = 3G_0kT \qquad (1')$$

The factor 7 used by Kuhn is an insignificant refinement of the factor 3.

The Influence of Viscosity in Calculating Elasticity

The calculation in the preceding section was based on the idea that the intermolecular statistics of an unstressed individual chain can be applied. However, in view of what has been said of the viscosity forces, this idea must be given up. It is very difficult to believe that the presence of viscosity forces at all points and under all conditions compensates for the viscosity corrections, because if we consider the statistics, and for no stress confine ourselves to a coördinating vector x, we find for the change in speed a mean value of:

$$\left(\frac{dx}{dt}\right) \qquad (7)$$

which increases with increase in the longitudinal factor x. Consequently, the heat motion in the more highly stretched states conflicts to a greater extent with the viscosity than it does in less highly stretched states.

To determine x in Equation 7, we introduce the previously mentioned principle of the constancy of the chain length. Designating the probability pertaining to lengths x to $(x + dx)$ by $f(x)dx$, we obtain:

$$f(x) = \text{const.}\, e^{-\frac{x^2}{B}} \qquad (8)$$

in which for the sake of brevity $2b^2Z = B$. A change in the chain length by the factor m corresponds to the same change of B; mB is substituted for the former B. If x is positive, then the mean value $\left(\frac{dx}{dt}\right)$ is naturally negative; that is, contrac-

tion is more likely to occur than extension, for according to Equation 8 the shorter lengths x are more probable, and a maximum when the length is zero (x being a component of the vector $[x, y, z]$!), according to the diffusion theory:

$$\left(\frac{dx}{dt}\right) = f'(x) \cdot g(x;\ B) \tag{9}$$

whereby the additional function $g(x;\ B)$ is derived from the invariance principle. From Equations 8 and 9, we get:

$$\left(\frac{dx}{dt}\right) = -\frac{2x}{B}\, e^{-\frac{x^2}{B}}\, g(x;\ B)$$

and for the transformation $x \longrightarrow mx$, $B \longrightarrow mB$ it follows that:

$$m\left(\frac{dx}{dt}\right) = \frac{2}{B}\, mx \left(e^{-\frac{x^2}{B}}\right)^m g(mx;\ mB)$$

Therefore

$$\left(e^{-\frac{x^2}{B}}\right)^m g(mx,\ mB) = e^{-\frac{x^2}{B}}\, g(x;\ B)$$

is independent of m.

The simplest way to satisfy this equation is to assume that:

$$g(x;\ B) = \text{const.}\ e^{-\frac{x^2}{B}} = \text{const.}\ \frac{1}{f(x)}$$

so that, for Equation 9, we obtain as the final equation:

$$\left(\frac{dx}{dt}\right) = \text{const.}\ \frac{f'(x)}{f(x)} = \text{const.}\ \frac{d \log_e f(x)}{dx} \tag{10}$$

and taking into account Boltzman's relation, $S = k \log_e W$, the equation becomes:

$$\left(\frac{dx}{dt}\right) = \text{const.}\ \frac{dS}{dx}$$

This leads to a proportionality between the mean contraction velocity and the elastic tension. It is important to note that for any chain length the contraction velocity, $\frac{d(mx)}{dt}$, is proportional to m, and therefore also to the chain length (mZ).

It is impossible to derive by direct mathematical methods the intermolecular statistics of the determinant forces. Instead, we recommend a method based on the idea that the hindrance to motion due to viscosity is equivalent to an interlacing effect.[3] The width of the mesh of this network is, therefore, not positively established, because the interference with motion does not set in abruptly, but gradually. To allow for this condition, the very long real chain may be considered to be composed of superimposed shorter chains of various lengths, and these lengths are given statistical weights of less than unity, so that the total weight at each point is exact unity. This concept of a superimposed structure has been borrowed from other fields of physics. In answer to objections to the reliability of this method, it should be pointed out that the observation in question is an alternative to the correct intermolecular statistics, which cannot be deduced. The intermolecular statistics for no stress, which up to now have been applied, are also used for the component parts out of which the structure is built up.

The weight function which belongs to the hypothetical chain lengths of l to $l + dl$ is $\varphi(l)dl$. Therefore

$$\int_0^\infty \varphi(l)dl = 1 \tag{11}$$

must be valid.

For the φ function, we assume the differential equation:

$$\frac{d\varphi(l)}{dl} = -c\left(\frac{dx}{dt}\right)\varphi(l) \tag{12}$$

in which the length x refers to the hypothetical chain length, so that:

$$\left(\frac{dx}{dt}\right) = c'l \tag{13}$$

Here it is assumed first of all that the length l in general extends in the direction of x. From Equations 12 and 13 we get:

$$d \log_e \varphi(l) = -cc'ldl$$

or integrated:

$$\varphi(l) = \text{const.}\, e^{-\frac{cc'}{2}l^2} \tag{14}$$

resulting in an incorrect law. At present the only proof of the validity of the fundamental differential Equation 12 is the failure of other hypotheses, as well as the fact that the requirements in Equation 11 are readily satisfied by Equation 12. A confirmation of Equation 12 will be possible only after the constants are determined and with the aid of correct intermolecular statistics.

In the use of Equation 14 for studying the problem of elasticity, all the partial existing chains, together with their partial weights for the determination of the entropy per unit volume, are required. In this way we obtain:

$$S = S_x + S_y + S_z;\ S_x = \overline{S_x(\alpha)}$$

$$\overline{S_x(\alpha)} = \iiint ds_x ds_y ds_z U(s_x s_y s_z \lambda) \int \frac{L}{l}\left(c_1 - \frac{x^2}{2b^2 Z}\right)\varphi(l)dl$$

where L is the total length of all chains per unit volume, α is the angle between the l and x directions, and S_y and S_z are derived in an analogous way.

$U(s_x s_y s_z \lambda)$ is the weight factor, still to be determined, which governs the distribution of the different degrees of stress s_x, s_y, s_z. The chain link number Z may be expressed as $Z = \frac{l}{l_0}$, so that Z refers also to the partial state. The rest of the calculation follows the example outlined on pages 57–58.

Although admittedly less precise, the method used here is a substitute for impracticable methods of calculation, and will give complete results; it is, in fact, a counterpart of the method used by Christiansen[4] for calculating the kinetics of reactions, as exemplified by its application to the diffusion theory.

This sketchy method of calculation will be carried out more precisely in the second part of this report, and will also be compared with the corrected molecular statistics.

The Intermolecular Statistics with Regard to Stresses

The problem of establishing the entropy-elasticity of rubber, as well as of related substances, on a quantitative basis led the author[5] in the first part of this work to deduce the differential equation:

$$\frac{d\varphi(l)}{dl} = -c\left(\frac{dz}{dt}\right)\varphi(l) \qquad (1)$$

At that time, however, the equation was based only on arbitrary assumptions, and we shall now prove its validity. $\varphi(l)$ was defined as a weight function which, because of its importance, warrants a review.

The rubber substance may be regarded as consisting of chain molecules, each of which is assumed to be very long so that the end-points may be disregarded. For the sake of simplicity it may be assumed that the chain is a part of the length l_0 of an infinite long chain molecule; it is further assumed that this part extends predominantly in one definite direction, which we designate as the z direction. Then, by starting from a fixed center and assuming an active length, l, which is shorter than l_0 and is characterized by the fact that by applying the already known intermolecular statistics for no stress to a part of this length, the actual elastic properties are thus obtained. However, in addition to this, virtual states with different l values must be imagined as superimposed in such a way that the lengths between l and $l + dl$ are apparently represented by the weight $\varphi(l)dl$. In this way it may be considered that the differential Equation 1 applies to the function $\varphi(l)$.

It should be pointed out first of all that it is not a question of superimposed states in the sense of wave mechanics, for an evaluation of the order of magnitude shows at once that such a quantum mechanics possibility is out of the question. Rather, one has to think in the present case of a statistically unarranged succession in the formation of the various active chain lengths, so that $\varphi(l)dl$ represents the mean fraction of time corresponding to the length interval of l to $l + dl$. Based on this concept, the relation of (l) is then readily established in so far as the influence of external stresses on the chain molecule is concerned, that is, in the sense of irregularly distributed transmissions of impulses.

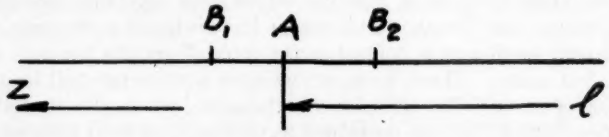

Figure 1

Naturally, only impulse transmissions in the positive or negative z direction are of interest. The actual active part of the chain molecule may be assumed to be confined between two individual impulse transmissions occurring in the positive and negative z direction. (See Fig. 1.)

The distance l is assumed to end at A, at which point an impulse transmission occurs in the positive direction. In the next instant an impulse transmission may occur at points B_1 or B_2, resulting either in an increase or in a decrease in the actual length l. Both possibilities are equally probable. It is less probable that an impulse transmission may occur simultaneously at points B_1 and B_2, with the result that the distance l will decrease just as if the impulse were transmitted only at B_2. In the final analysis we find that the active chain length is more likely to decrease than to increase, as is shown fundamentally by Equation 1. It is quite evident that $\left(\frac{dz}{dt}\right)$ still enters into the coefficient of this differential equation, that is, the mean relative velocity of the observed points of the chain molecule, since the relative motion to accomplish these impulse transmissions is naturally determinative. That the effect considered here is the cause of the observed elasticity follows from

the principle of equality of action and reaction, since the impulse transmissions discussed involve equal and opposite impulse transmissions acting around the chain molecule.

The problem of deducing intermolecular statistics for the stresses appears in principle to be solved by the differential Equation 1. However, certain objections remain to be answered, *e. g.*, due to the smaller impulse transmissions which are always present, only very short effective chain lengths play a part, and these because of their small chain member number, have no relation to the observed elasticity. Against this it may be pointed out that only relatively infrequent impulse transmissions above a certain minimum are concerned, and this minimum is governed in the following way. An impulse can be conceived as the product of force and time. If we use for the force the elastic tension, calculated from statistics for no stress, then, for the majority of (thermal) impulse transmissions we obtain an effective time duration, which is short compared to the mean time interval between two such events. All of these impulse transmissions may be disregarded in a first approximation. The few remaining impulse transmissions of considerable magnitude determine the differential equation, *i. e.*, for the mesh-width of our viscosity-interlacing effect.

Some conclusions based on this Equation 1 have already been made in the first part of this work. However, up to now it has been impossible to determine the coefficient c.

The Determination of the Coefficient c

As is obvious from the foregoing discussion, the occurrence of impulse transmissions simultaneously in the same direction at points B_1 and B_2 has a determinant influence on the coefficient c, and therefore, in general, the closeness of the simultaneous impulse transmissions that occur at greater distances. It is therefore necessary to know for a given relative velocity the algebraic sum of all impulse transmissions per unit length. This means knowledge of a viscosity coefficient.

The viscosity coefficient is defined as the force of gravity per unit area at a velocity of fall of unity. There, however, we have a stress per unit length with relative velocity of unity. The dimension is the same, yet no direct relation between this coefficient and a viscosity coefficient as ordinarily defined without an arbitrary additional assumption, *e. g.*, the distance between adjacent molecules, *i. e.*, an outer limiting condition of the range of flow, or differential state of flow.

It shows that the introduction of the viscosity coefficient, indicated by y, is also dimensional in order. This dimension is:

$$\left[\frac{\text{Force} \times \text{Time}}{\text{Area}}\right]$$

The dimension of the coefficient c in the differential equation is:

$$\left[\frac{\text{Time}}{\text{Area}}\right]$$

so that the ratio of the two factors has the dimension of a force. It is easy to identify this force as the entropy-elastic tension s of the chain molecule in question:

$$c = \frac{\eta}{s} \tag{2}$$

Hence, the differential Equation 1 is:

$$\frac{d\varphi(l)}{(dl)} = -\frac{\eta}{s}\left(\frac{dz}{dt}\right)\varphi(l) \tag{3}$$

In proving Equation 2 it is necessary to refer to Fig. 1. The distance AB_2 may be expressed by the differential (dl). The unit length is long compared to this distance. In this case the probability of an impulse transmission at the distance running from the left to point A must be compared with the probability of one running from the left to point B. These two probabilities differ however (per unit time) by $\frac{\eta\left(\frac{dz}{dt}\right)dl}{s}$, for the impulse transmission per unit length and unit time is $\eta\frac{(dz)}{(dt)}$, while the total impulse transmission per unit length is equal to S.

Although our η is defined otherwise than as a normal viscosity coefficient, its magnitude can be estimated by extrapolation of the recorded viscosity data of plastic high molecular substances. A correct method of determining η will be offered in the near future.

The Velocity of Relative Motion

As already stated in the first part of this report, the mean relative velocity $\left(\frac{dz}{dt}\right)$ is assumed to be proportional to the length l:

$$\left(\frac{dz}{dt}\right) = c_1 l \tag{4}$$

The magnitude c_1 is fixed by the relations which, in general, determine the duration of irreversible reactions outside the range of influence of quantum effects. Therefore in determining c_1, one has to rely on theories of diffusion, heat transmission, relaxation, etc. Since this also holds true for the observed viscosity coefficient, it may be assumed that η and c_1 cannot be determined individually, but only as a combination of the two magnitudes, perhaps the product of $c_1\eta$. This, however, is sufficient for calculations based on Equation 1 since by substituting Equations 4 and 2, Equation 1 becomes:

$$\frac{d\varphi(l)}{dl} = -\frac{c_1\eta}{s} l\varphi(l) \tag{5}$$

It has already been shown in the first part of the present work that such a method leads to a Gauss curve of errors for $\varphi(l)$.

The influence which the presence of true points of interlacing, *e. g.*, in vulcanized rubber, exerts on the elastic properties, and which according to experiments is considerable, will be fully appreciated only when $c_1\eta$ is determined. This subject is being withheld for the third part of this work.

I wish to express to Professor Mark my sincere thanks for his encouragement and assistance in this work.

References

[1] Meyer and Ferri, *Helv. chim. acta*, **18**, 570 (1935); Guth and Mark, *Monatsh.*, **64**, 93 (1934).
[2] Kuhn, *Kolloid-Z.*, **76**, 258 (1936).
[3] Dostal, *Monatsh.*, **71**, 144 (1938).
[4] *Z. physik. Chem.*, **33B**, 145 (1936); **37B**, 374 (1937).
[5] In the first part of this work, this z direction was designated as the x direction; t is negative time so that the mean value is positive.

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Isothermal and Adiabatic Stress-Strain Curves of Vulcanized Rubber

V. Hauk and W. Neumann

Introduction

The stress-strain diagram of rubber has been the subject of a large number of investigations, including those of Röntgen,[1] Gough, and Joule in the nineteenth century, those on isothermal phenomena by Meyer and Ferri,[2] and Wiegand and Snyder,[3] and most recently those on adiabatic phenomena of Ornstein, Eymers, and Wouda.[4]

The investigations of Meyer and Ferri are concerned chiefly with the dependence of the stress-strain phenomena on the temperature, and they confirm experimentally the hypothesis that within a certain range of temperature and with highly vulcanized samples, the stress is proportional to the absolute temperature, *i. e.*, $S = aT + b$. At lower states of vulcanization this proportionality does not hold true. The work of Ornstein and his collaborators, which is frequently cited in the literature, is concerned with the phenomena which take place when raw rubber and weakly vulcanized rubber are stretched adiabatically; that of Wiegand and Snyder is concerned chiefly with a thermodynamic interpretation of stress-strain curves obtained experimentally.

Now in spite of the fact that stress-strain curves of rubber have been determined so frequently, particularly under isothermal conditions, these measurements are for the most part of limited value, since the chemical nature of the types of rubber employed is not described definitely. Then again in most cases little attention was paid to the difference between isothermal and adiabatic stretching.

In view of these facts, it seemed desirable to throw further light on the problem by obtaining stress-strain curves of one particular well-defined material. The object of the present work was then:

1. To obtain true isothermal stress-strain curves as a function of the degree of vulcanization and as a function of the temperature, and thus to study stresses as a function of temperature.
2. To obtain data on the same vulcanizates under adiabatic conditions.
3. To compare the stress-strain results under isothermal conditions with those under adiabatic conditions.

Isothermal Extension of Rubber

To obtain a truly isothermal stress-strain curve, the samples in the form of strips, of the same dimensions in all cases, were loaded with various weights, and the changes in the length between two marks were recorded. As experimental material a series of vulcanizates prepared by the Hungarian Rubber Works was used; likewise samples prepared especially for the purpose were offered by the Austrian Semperit Works for study, and the authors take this occasion to express their deep appreciation to these two firms for their willingness to furnish the samples.

The eight samples from the Hungarian Rubber Works were prepared from the base mixture:

Crepe	100
Accelerator	10
Stearic acid	1
Zinc oxide	5

by adding the following proportions of sulfur:

Sample No.	Sulfur
1	1
2	2
3	3
4	4
5	5
6	6
7	7
8	8

The two samples from the Semperit Rubber Works were prepared from a simple rubber-sulfur mixture containing 8 per cent of sulfur, vulcanized for 60 and 90 min., respectively, at 180° C., *i. e.*, to the extent that sample No. 1 contained 2 per cent of combined sulfur and sample No. 2 contained 6 per cent of combined sulfur.

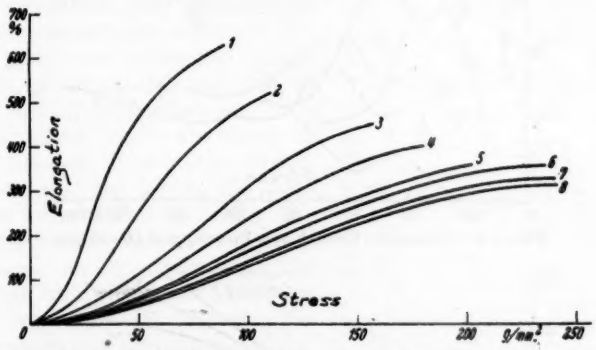

Figure 1—Isothermal Stress-Strain Curves of Vulcanizates Nos. 1 to 8 at Room Temperature (21° C.) (See Table I)

By obtaining stress-strain curves of the first set of eight samples, *i. e.*, of rubber at various stages of vulcanization, the group of curves shown in Fig. 1 was obtained. The relatively low extensibility of vulcanizates with high sulfur contents, an already well-known fact, is evident. If an intersecting line is drawn through these curves at any given stress and the resultant values are plotted, a curve of the elongation as a function of the degree of vulcanization is obtained. Such curves are illustrated in Fig. 2. It is evident that the elongation depends to an especially great extent on the sulfur content when the latter is below 4 per cent, and to a relatively slight extent when the sulfur is above 4 per cent. At the higher percentages, this transition range is not so clearly marked, and the curves are flatter.

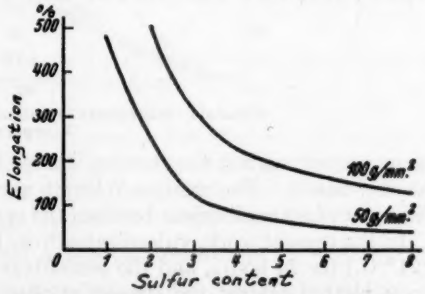

Figure 2—Dependence of the Elongation at Constant Stress on the Sulfur Content

Changes in Loaded Samples as a Function of Time

In a very interesting and detailed investigation of weakly vulcanized rubber stretched under isothermal conditions, Kirsch[5] has reported that a series of samples of vulcanized rubber, all of the same dimensions but loaded to different degrees, showed, after being subjected to certain stresses for 50 hours, changes in their original elongations, and that when the percentage increases in length after 50 hours

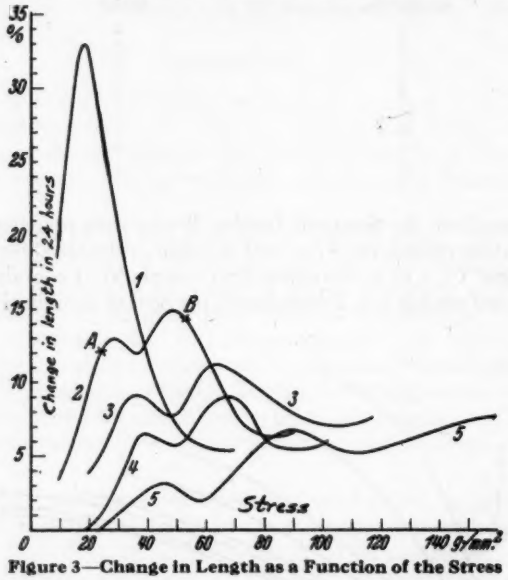

Figure 3—Change in Length as a Function of the Stress

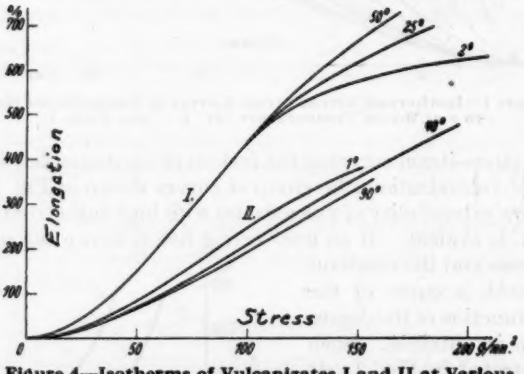

Figure 4—Isotherms of Vulcanizates I and II at Various Temperatures

were plotted against the stresses, curves having two maxima at different stresses were obtained. The changes in length were attributed by Kirsch to the slow establishment of an equilibrium between the crystalline and liquid phases in the rubber.

In the present work, vulcanizates Nos. 1 to 5 were stressed at room temperature (21° C.) for 24 hours, and the percentage increases in length during the 24 hours were plotted against the stresses applied. The group of curves for the samples vulcanized to various degrees is shown in Fig. 3. A lowering of the maxima and

their shift to higher stresses with increase in the degree of vulcanization are evident on the one hand; a mutual approach of the maxima at the lower states of vulcanization, to the extent that in the case of the vulcanizate containing 1 per cent of sulfur both maxima coincide as a single high maximum, is evident on the other hand.

On the assumption that these maxima can be explained in the same way as the maxima in the isothermal stress-strain curves of latex,[6] *i. e.*, by the beginning of crystallization and the accompanying hardening, x-ray photographs of points *A* and *B* in Fig. 3 were made. These roentgenographs showed the expected result, *viz.*, no evidence of crystallization for point *A* previous to the maximum and a fiber diagram for point *B* after the maximum.

The Dependence of the Stress-Strain Curve on the Temperature

In this investigation the two vulcanizates prepared by the Semperit Rubber Works were chosen as examples of mildly and highly vulcanized rubber. For the sake of clearness, the less highly vulcanized sample was tested at 2°, 25°, and 50° C., the more highly vulcanized sample was tested at 10°, 40°, and 90° C. As in all other stress-strain measurements under isothermal conditions, the stress-strain curves were obtained with strips of like dimensions, which were stressed to various degrees. An air thermostat was used to maintain a constant temperature.

The experimental results are shown in Fig. 4. In the case of the more highly vulcanized sample, the higher the temperature, the lower the curve on the diagram, *i. e.*, the stress increased with increase in temperature; on the contrary, in the case of the less highly vulcanized sample a change in temperature did not alter the stress-strain curve over a wide range of low elongations, and only at relatively high elongations do the three isothermal curves spread, and then in a direction opposite to that for the more highly vulcanized sample.

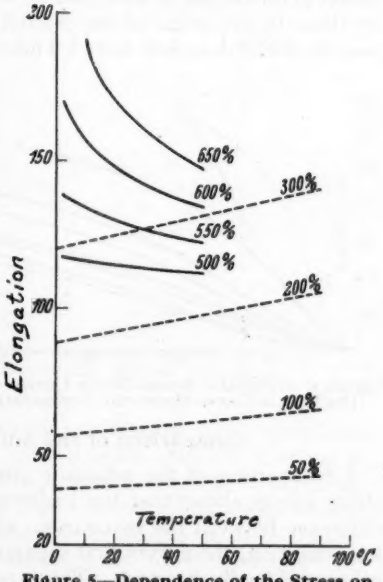

Figure 5—Dependence of the Stress on the Temperature at Constant Elongation (the Broken Lines Represent Vulcanizate II, the Solid Curves Represent Vulcanizate I)

These phenomena become particularly evident if the stresses are plotted as a function of the temperature, as shown in Fig. 5, whereby it becomes clear that in the case of the more highly vulcanized sample the proportionality between stress and temperature required by theory actually holds true. In the case of the less highly vulcanized sample, the relation is just the opposite at higher elongations, in fact, the higher the elongation, the more pronounced is this effect—a phenomenon which is easily explained on the assumption that crystallization sets in, with its accompanying hardening effect, in the case of the less highly vulcanized rubber. Further experiments with rubber vulcanized to a still less degree are in progress.

Rubber Stretched under Adiabatic Conditions

When rubber is to be stretched in a strictly adiabatic way, the rates of extension which must be applied are so great that the results can be recorded only by a cine-

matographic method. The apparatus used for making the stress-strain measurements was based, as was that of Ornstein, Eymers, and Wouda,[4] on the pull of a rubber band by a spring. If two marks are made on the spring and also on the rubber, it is possible, after calibration of the spring, to measure the stress applied to the rubber by the distance between the marks on the springs, and to measure the elongation by the distance between the marks on the rubber. This stress-strain relation was registered by means of films with a 16-mm. film camera. The film was then projected, and the desired data were obtained by measuring the distances between marks on the projected reproduction. Naturally the same rate of stretching was maintained in all experiments. The time of stretching was less than one second. The adiabatic stress-strain curves derived by this method for the samples of various degrees of vulcanization comprised the group shown in Fig. 6. The most surprising feature is the much flatter trend of these curves compared with the isothermal curves, and the only slightly curved or almost straight ascent. No breaks in the curves, as described by Ornstein, Eymers, and Wouda,[4] and attributed by them to the point where crystallization commenced, were evident, and it is possible that the authors were led into errors as a result of vibration of the spring.

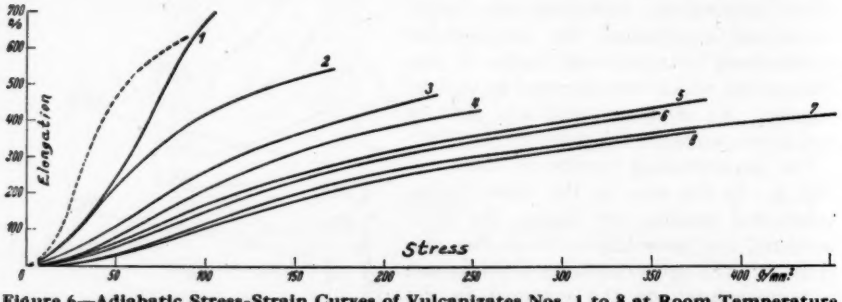

Figure 6—Adiabatic Stress-Strain Curves of Vulcanizates Nos. 1 to 8 at Room Temperature (the Broken Curve Shows the Comparative Course of the Isotherm of Vulcanizate No. 1)

Comparison of the Adiabatic and Isothermal Curves

A comparison of the adiabatic stress-strain curves with the isothermal stress-strain curves shows that the higher the state of vulcanization, the greater is the difference between the two curves, whereas in the case of relatively low states of vulcanization, the curves first separate, then at higher elongations approach each other, and finally intersect. This is particularly evident in the case of sample No. 1 in Fig. 6 and sample No. 1 (2 per cent sulfur) in Fig. 7. The configuration of these adiabatic curves cannot be explained by purely thermodynamic means. Although the adiabatic curves would necessarily lie below the isothermal curves as observed (provided that the elasticity of rubber is regarded as a statistical effect in an analogous way to the behavior of a gas), nevertheless, the effects actually observed are too great to be explained in this way. When stretched adiabatically, rubber would have to reach elevated temperatures (above 100° C.) which are obviously impossible. Furthermore in the case of weakly vulcanized rubber, in which crystallization and intermolecular forces would predominate over the statistical effect, as is obvious from the stress-temperature curves, the difference between the adiabatic and isothermal curves would necessarily disappear, or would be appreciable only at relatively high elongations and then in the opposite sense. The great difference between the adiabatic curves and isothermal curves can therefore be explained only on the basis that the rate of stretching is of decisive influence on the extent to which

the molecular chains are extended themselves. It would seem at first thought that during rapid stretching, chains are ruptured while they are still in a coiled state, which would result in a hindrance the same as that of further vulcanization, a point of view quite in harmony with the views of Dostal[7] on the quasi-network effect of viscosity.

A study of the group of adiabatic curves and the corresponding group of isothermal curves for the various degrees of vulcanization makes it evident also that in general an adiabatic curve for any particular state of vulcanization is nearly the same as the isothermal curve for a more advanced state of vulcanization. Consequently, in the upper part of the curve of the less highly vulcanized sample there is an intersection, because crystallization causes an inflection in the isothermal curves, whereas in adiabatic stretching crystallization does not begin until higher elongations are reached. Furthermore, the almost linear course of the adiabatic curves can be explained by the prolonged after-effect of the resulting intermolecular forces.

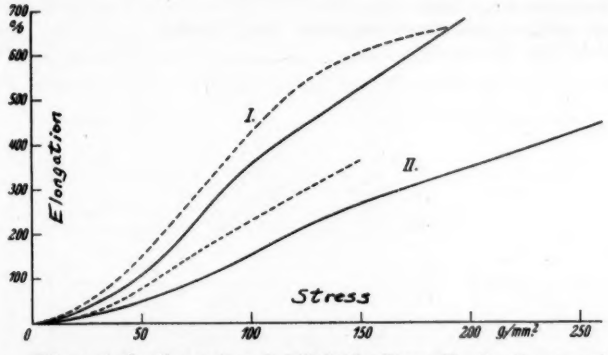

Figure 7—Isothermal and Adiabatic Stress-Strain Curves of Vulcanizates I and II at Room Temperature (the Broken Curves Are the Isotherms)

To explain these phenomena more fully, further experiments were carried out with various rates of stretching. It is also quite possible that the changes in elongation with time, observed in the case of the isothermal curves, can be explained in a similar manner. In virtue of the opening of the individual coiled chains, changes in length occur as time goes on, and under some conditions these changes may be prevented by the crystallization which has set in and which thereby stiffens the whole system. In this way it is possible to explain satisfactorily the occurrence of maxima. In no case do any actual flow phenomena play a part, for the permanent irreversible elongation is not related in any way to the change in length. In the case of relatively high states of vulcanization, the maxima occur at higher stresses as a result of subsequent crystallization, while at the same time the whole phenomenon is less clearly defined because shorter chains take part in the process.

Résumé

1. Isothermal stress-strain curves of vulcanizates of known composition were determined, and the fact was established that extensibility depends on the sulfur content.

2. The changes of length with time of rubber samples of like dimensions and vulcanized to various states were measured under different stresses.

3. The stress as a function of temperature of a mixture of definitely known chemical composition and vulcanized to various states was determined.

4. The adiabatic stress-strain curves of vulcanizates of known composition were obtained by means of a special stress-strain apparatus.

5. The isothermal and adiabatic measurements are compared with one another and the results are discussed.

Acknowledgment

The authors take the occasion to offer Professor Mark their sincere thanks for the interest which he showed in the work and for his valuable advice. Likewise, the authors thank General Director Messner of the Semperit Works for responding so generously in preparing samples of rubber for them.

References

[1] Röntgen, *Ann. Physik*, **159**, 601 (1876).
[2] Meyer and Ferri, *Helv. chim. acta*, **18**, 570 (1935).
[3] Wiegand and Snyder, *Trans. Inst. Rubber Ind.*, **10**, 234 (1934).
[4] Ornstein, Eymers, and Wouda, *Proc. Acad. Amsterdam*, **32**, 1235 (1929).
[5] Kirsch, *Dissertation*, Berlin, **1937**.
[6] Hintenberger and Neumann, *Naturwissenschaften*, **26**, 13 (1938).
[7] Dostal, *Österr. Chem.-Ztg.*, in press.

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Studies on Deproteinized Rubber

V. Effects of Several Proteins

T. Ōkita

It has been reported that rubber cures slowly when the protein in the rubber is removed, and similar results have been obtained in the author's experiments (Reports 1 and 4). As the phenomenon has relation to evolution of hydrogen sulfide during vulcanization, several experiments were carried out concerning these points.

Vulcanization Test

7.5 parts of sulfur were mixed with 92.5 parts of washed smoked sheet or deproteinized rubber, and 5 parts of albumin, glutamic acid, hemoglobin, and gelatin, respectively, were added to the latter. These 6 mixes were cured in sheets 1.2 to 1.4 mm. thick in a press at 148° C. Tensile strengths of these samples are shown in Fig. 1.

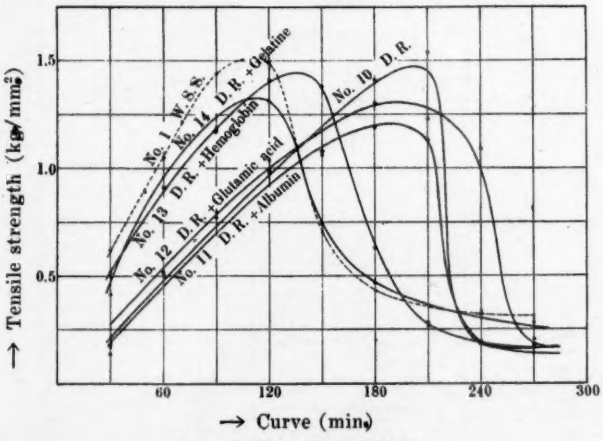

Figure 1—Cure Test (148° C.)

The curing velocity of rubber is accelerated by these proteins. The effect is most pronounced in the case of gelatin, followed by hemoglobin and albumin. Glutamic acid has a slight effect on cure. The deproteinized rubber mixed with gelatin cured in almost the same time as the mixture of washed smoked sheet.

Evolution of H_2S from Uncured Mixes

The six mixes described were cut into small granules (ca. 1 cc.), and amounts of H_2S evolved on heating at 148° C. in a stream of carbon dioxide (Fig. 2) measured.

The evolution of H_2S per hour was a maximum in the case of washed smoked sheet, followed by the mixes of hemoglobin, gelatin, deproteinized rubber, albumin, and glutamic acid. The evolution of H_2S was a maximum after 30 to 60 min. before the maximum tensile strength was reached. It was assumed that some intimate relation would exist between the changes of tensile strength and the evolution of hydrogen sulfide.

The total amount of hydrogen sulfide evolved from deproteinized rubber was smaller than that from washed smoked sheet, and the variation of the amount per hour was also smaller than that from the latter rubber. When some of the proteins were mixed in deproteinized rubber, the amount of hydrogen sulfide evolved per hour increased at the beginning of heating and decreased after several hours; the total amount of hydrogen sulfide was smaller than in the blank test.

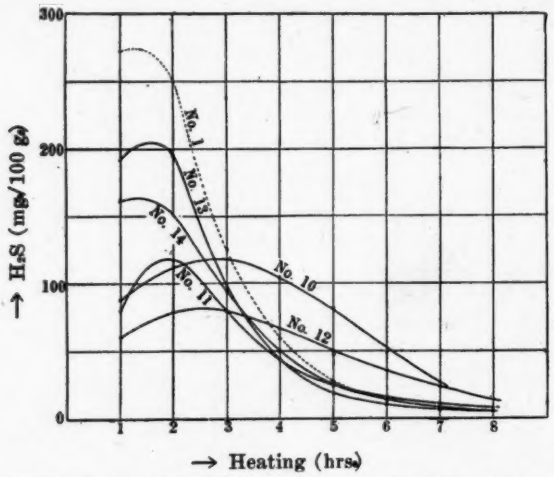

Figure 2—H_2S Evolution from Uncured Samples (148° C.)

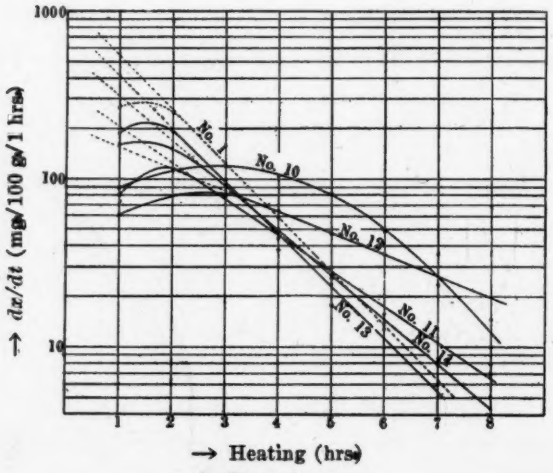

Figure 3

It may be concluded from these facts that proteins do not increase the amount of hydrogen sulfide evolved from rubber mixtures during cure, but accelerate the speed of evolution of hydrogen sulfide at the beginning of cure.

When the total amount of hydrogen sulfide evolved after t hours is expressed by x, we obtain the following empirical formula:

$$x = C\,(1 - e^{-b\,(t-a)})$$

where C, b, a are constants. This formula will be discussed in another report.

Heat-Resisting Properties and Evolution of Hydrogen Sulfide

Three of the mixes described above were cured to their optimum states, and to under-cures (ca. 20 min. less than optimum) as sheets 1.2 to 1.4 mm. thick. Test-pieces of dumb-bell shape were punched from these sheets, and heated at 130° C. (Fig. 4) in a stream of carbon dioxide. The remaining parts of the sheets

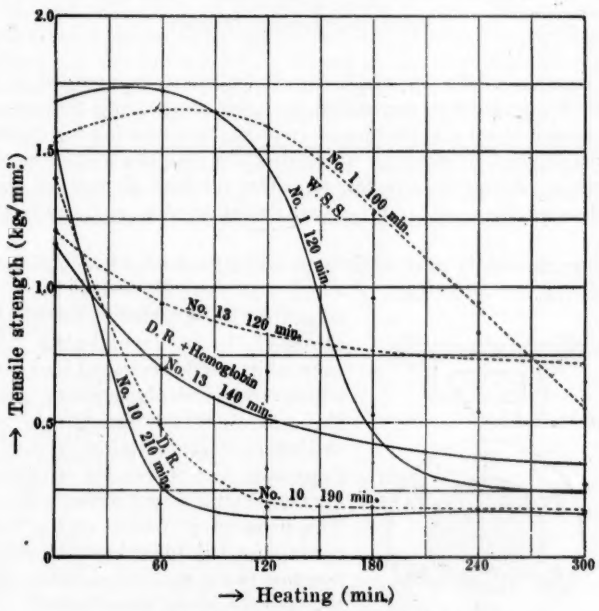

Figure 4—Heating Test (130° C.)

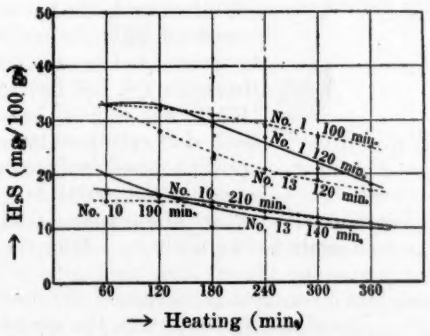

Figure 5—Evolution of H_2S from Cured Rubbers (130° C.)

were cut into small granules (ca. 1 cc.) and the amounts of hydrogen sulfide were measured by heating in a stream of carbon dioxide at 130° C. (Fig. 5).

The amount of hydrogen sulfide from deproteinized rubber was smaller than that from washed smoked sheet, and was increased by hemoglobin.

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 14, No. 12, pages 231–232 December, 1938.]

The Permeability of Organic Substances to Water

E. Badum

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Although organic substances are in the ordinary sense regarded as waterproof, actually they are somewhat permeable to water vapor, and this permeability is sufficient to render them inapplicable as covering or sheathing for cables. In view of this, it was decided to study in a quantitative way the phenomenon of permeability to water of organic substances. The method chosen for making these measurements and the results obtained are described in a brief way in the following paragraphs.

The first measurements were made with an apparatus which consisted of a hemispherical bell jar, the open part of which was carefully sealed by a sheet of the substance to be tested. To this bell jar was attached, by a ground-glass connection, a tube which could be closed by a stopcock, and which contained phosphorous pentoxide. In this way the vapor pressure of water within the bell jar was maintained at zero. The small apparatus was suspended in a constant-temperature chamber saturated with water vapor. The increase in weight of the weighing tube containing the phosphorous pentoxide was a measure of the amount of water which diffused through the sheet being tested.

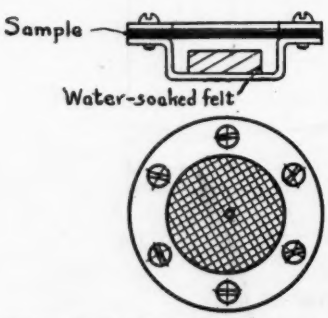

Figure 1—Measurement of Permeability to Water

$$k = \frac{d.\ m.}{q.\ p.\ t.}$$

k = permeability
d = thickness (cm.)
q = area (sq. cm.)
m = loss in weight (grams)
p = vapor pressure in cell (mm. of Hg)
$p = f(T)$
t = time (hours)

In the course of the investigation we turned our attention to the few publications which are concerned with the problem of permeability to water, and as a result the apparatus of Herrmann (cf. *Bell Laboratories Record*, **13**, 45 (1934)) was adopted as an especially suitable method of experimentation (see Fig. 1). This apparatus consists of an aluminum cell, in which a piece of felt soaked in water is placed. The open part of the cell is sealed with a sheet of the material to be tested, which is cemented to the cell or held against it by pressure. After the cell is weighed, it is placed in a desiccator containing phosphorous pentoxide or calcium chloride as drying agent. To maintain a constant temperature, the desiccator is placed in a thermostat (see Fig. 2). At definite time intervals, the loss of weight of the cup is determined by weighing it. This loss of weight represents the amount of water which has diffused through the surface of the test-sheet. The amount of water m (in grams) which diffuses through the test-sheet is proportional to the area q (in sq. cm.) of the test-sheet, to the time t (in hours), and to the difference in vapor pressure between the interior of the cell and the desiccator, and is inversely proportional to the thickness d (in cm.) of the test-sheet. A factor k, which depends

on the substance tested, also enters into the formula; this factor represents the specific permeability to water vapor of the sheet. The resulting expression:

$$m = k \frac{q \cdot t(p - p_0)}{d}$$

corresponds to the so-called Fick's law for the diffusion of gases. The diffusion constant k is derived from the relation above:

$$k = \frac{m \cdot d}{q \cdot t(p - p_0)}$$

This formula is valid only if the water passes in the form of vapor through the test-sheet. As proof of the correctness of this assumption it might be mentioned that it is immaterial, as far as the results are concerned, whether the sample is immersed directly in water or in an atmosphere saturated with water vapor.

Calculations by this formula from data on various organic substances gave results which are summarized in the table below. A diffusion constant of 20×10^{-8}, for example, signifies that 20×10^{-8} gram of water passes per hour, under a pressure of 1 mm. of mercury, through a cube 1 cm. on each side.

PERMEABILITY OF ORGANIC SUBSTANCES TO WATER

Substance	$k \times 10^{-8}$
Cellulose triacetate (with plasticizer)	326
Cellophane	200
Cellulose acetate	160
Cellulose triacetate	84
Igelit MP (with plasticizer)	22
Igelit PCU (with plasticizer)	20
Stabol (polyacrylic acid ester)	16
Buna-S (vulcanized, without fillers)	11
Buna-S (vulcanized, with 25 vol.-per cent of black CK 3)	10
Buna-S (vulcanized, with 25 vol.-per cent of talc)	3
Perduren	2–11
Benzylcellulose	8–10
Rubber (vulcanized, without fillers)	8
Rubber (vulcanized, with 25 vol.-per cent black CK 3)	8
Rubber (vulcanized, with 25 vol.-per cent of talc)	2.5
Polystyrene	3.8
Styroflex	2.7
Hard rubber	1.5
Gutta-percha	1.5
Cellophane (weatherproof)	1.5
Asphalt	1.4
Igelit PC	1.1
Igelit PCU	0.8

It is evident from the data in the table above that cellulose derivatives are most permeable to water, except for benzylcellulose and "weatherproof" Cellophane. The mixtures containing thermoplastics show values lying between 10 and 20, while the pure thermoplastics are least permeable to water, *i. e.*, have $k \times 10^{-8}$ values around 2.

These results lead to the general rule that plasticizing agents increase the permeability of the base substances to water. This phenomenon can perhaps be attributed to the polar nature of the plasticizing agents. A few other industrial organic materials are included, *e. g.*, asphalt, gutta-percha, and hard rubber. Of special interest are the values of Buna-S and rubber. Vulcanized Buna-S containing no fillers is more permeable to water than is natural rubber and, according to measurements by Dr. Roelig of Leverkusen, the values of Perbunan and Levulkan are of the same order of magnitude as those of rubber.

The question naturally arises as the manner in which the permeability to water of Buna and of rubber is changed by the addition of fillers.

To two base mixtures containing 100 parts of Buna and natural rubber, respectively, and 1 part of sulfur, 5 parts of zinc oxide, and 1 part of Vulkazit AZ, were added 25 per cent by volume of various fillers. The sheets prepared from these vulcanizates were tested by the method described above, and it was found that the various fillers had, in general, the same effect on the permeability of rubber as they did on the permeability of Buna. The particular fillers which were tested diminished the permeability of rubber and of Buna to water.

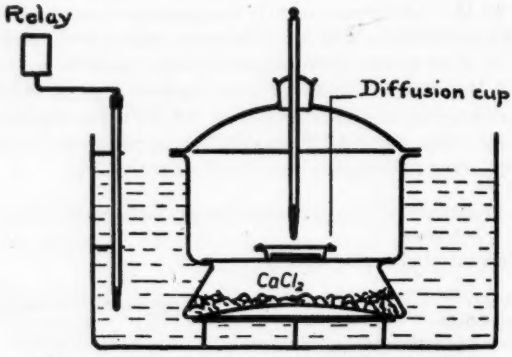

Figure 2—Measurement of Permeability to Water

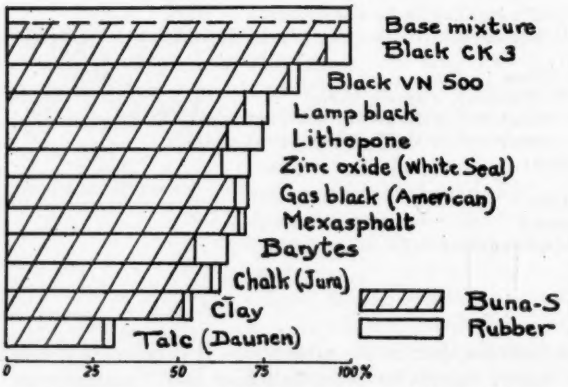

Figure 3—Influence of Fillers on the Permeability to Water

Figure 3 shows the changes in the diffusion coefficients of the mixtures loaded with 25 per cent by volume of the fillers. The permeability to water of each of the two base mixtures is assigned a value of 100. The permeability of the base mixtures is changed least of all by the three carbon blacks, as is also evident in the foregoing table of absolute $k \times 10^{-8}$ values. The other fillers which were investigated reduced the permeability to water to values between 50 and 75 per cent of those of the base mixtures. The effect of talc as a filler is remarkable in that it lowered the permeability of the base mixtures to values less than 30 per cent of those of the base mixtures themselves.

However, the addition of substances which are known to be water-repellents, *e. g.*, paraffin, aluminum stearate, and zinc stearate, to mixtures already containing talc, does not, as shown by experiments, further reduce the permeability to water, at least to any practical extent.

It should be mentioned that all measurements were made at 25 ± 1° C. Measurements carried out at other temperatures showed that permeability to water depends to a very large extent on the temperature; however, it is impossible at this time to give any further information regarding the relation between permeability and temperature.

The chief result of the series of experiments which have been described is perhaps the conclusion that no organic substance has zero permeability to water. This is probably attributable to the fact that organic substances are composed of more or less large molecules, whereas metals, *e. g.*, lead, which have been proved to be absolutely impermeable to water, have an atomic lattice throughout their mass.

Literature

Schumacher and Ferguson, Diffusion of Water through Rubber, *Ind. Eng. Chem.*, **21**, 158 (1929).

Herrmann, Diffusion of Water through Organic Insulating Materials, *Bell Laboratories Record*, **13**, 45 (1934).

Taylor, Herrmann, and Kemp, *Ind. Eng. Chem.*, **28**, 1255 (1936).

Kline, *J. Research Nat. Bur. Standards*, **18**, 235 (1937).

Badum, Leilich, *Carlswerk-Rundschau*, No. **22**, 13 (1938).

[Reprinted from the Journal of the Society of Chemical Industry, Japan, Vol. 41, Supplemental binding No. 6, pages 205–207B, June, 1938.]

Influence of Copper on Rubber

VII. Effects of Metallic Salts on the Evolution of Hydrogen Sulfide

T. Ōkita

I have reported in former reports (Parts 4 and 6) that the effects of copper and other metallic compounds on vulcanized rubber can be explained by the formation of acids during vulcanization, and by the prevention of the evolution of hydrogen sulfide from vulcanized rubber by these acids. In the present work the author verified these suppositions by some experiments.

Evolution of Hydrogen Sulfide from Uncured Rubber

Five grams of mixes consisting of 100 parts of pale crepe, 8 parts of sulfur, and 1 to 5 parts of silver phosphate or sulfate were cut into small granules (ca. 1 cu. mm.) and the granules kept separate by a small amount of calcined silica powder. The samples were put in the apparatus shown in Fig. 1, the temperature of the

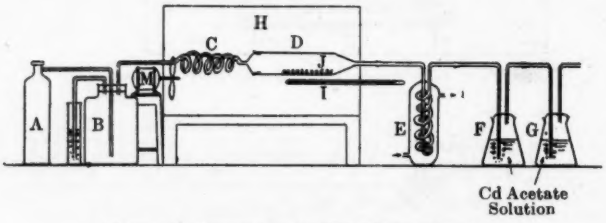

Figure 1—Apparatus of H_2S Determination

A.	CO_2 bomb	F.	H_2S absorber
B.	Gas tank	G.	H_2S absorber
C.	Preheater	H.	Air thermostat
D.	Heating part	I.	Thermometer
E.	Gas cooler	J.	Sample

thermostat being at 144° C. Carbon dioxide was passed through the inner part, and the hydrogen sulfide evolved from the rubber was absorbed by a solution of cadmium acetate, which was titrated by iodimetry and the amount of hydrogen sulfide was thus determined (Fig. 2).

The evolution of hydrogen sulfide from unvulcanized rubber during heating was depressed by a small amount of silver salt and was increased by a larger proportion. The maximum point of evolution in unit time was shifted by the silver salt. These two phenomena are similar to the curing curves of Report 6.

Evolution of Hydrogen Sulfide from Cured Samples

Mixtures consisting of 100 parts of pale crepe, 8 parts of sulfur, and 1 part of magnesium phosphate, zinc phosphate, lead phosphate, silver phosphate, and silver sulfate, respectively, were vulcanized in a press at 144° C. (steam pressure 3.5 kg. per sq. cm.) to their optimum cures. Ring samples were punched from the sheets of 4-mm. thickness and submitted to a heat test. The remaining parts were cut into small granules (ca. 1 cu. mm.) and the amount of hydrogen sulfide evolved by heating (Table I, Fig. 3) was measured.

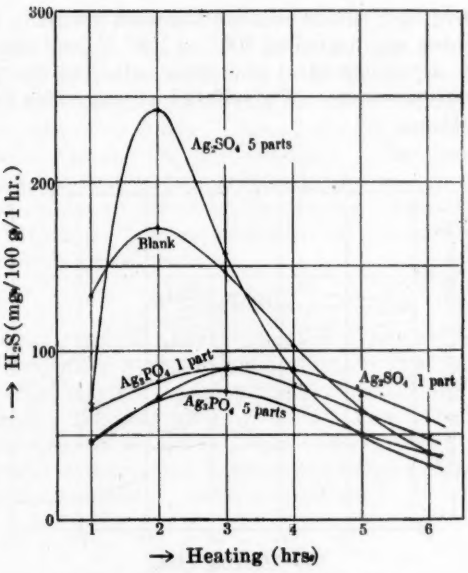

Figure 2—H_2S 144° C. Uncured Samples

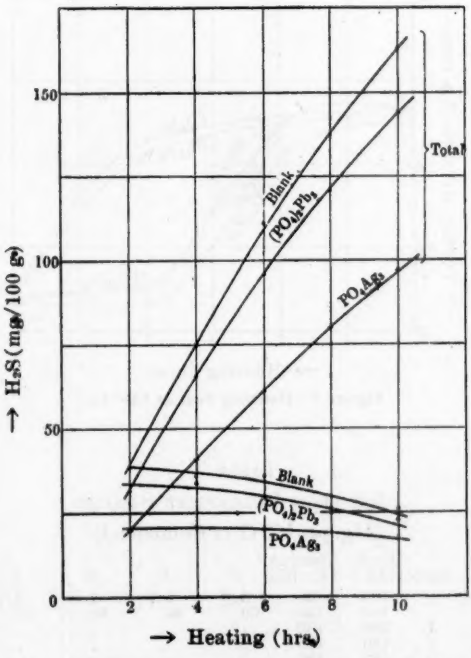

Figure 3—Evolution of H_2S from Cured Rubber (130° C.)

The amount of hydrogen sulfide evolved decreased gradually with lapse of time when the cured rubber was heated at 100° or 130° C. and also by addition of a metallic salt. This depressing effect of metallic salts was strong when the alkali property of the metals was weak. The sulfate is stronger than the phosphate even with smaller proportions.

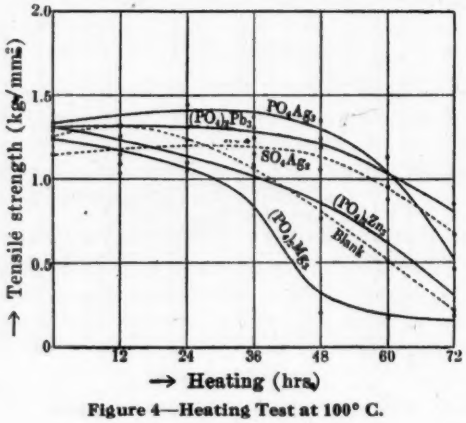

Figure 4—Heating Test at 100° C.

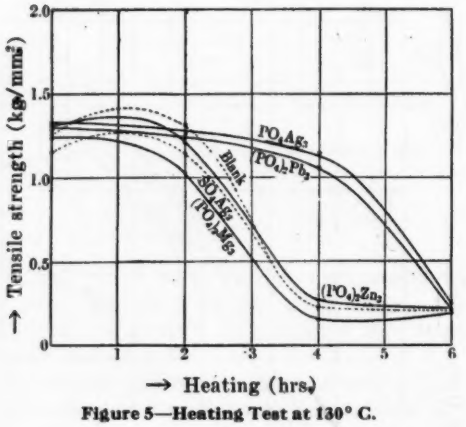

Figure 5—Heating Test at 130° C.

TABLE I

H_2S FROM VULCANIZED SAMPLES

(Mg. per 100 G. of Compound)

No.	Comp.	Parts	Cure (Min.)	Heating ° C., Hrs.	2	4	6	8	10	Total Mg. per 8 Hrs.
0	.....	.	160	100	3.0	2.7	2.8	2.9	2.5	11.4
0	.....	.	160	130	39	36	36	26	26	137
6–B	Ag_2SO_4	1	240	130	..	..	..	..	..	52
12–B	$Mg_3(PO_4)_2$	1	160	130	..	..	..	..	..	136
14–B	$Zn_3(PO_4)_2$	1	180	130	..	..	..	..	..	139
15–B	$Pb_3(PO_4)_2$	1	200	130	32	34	30	25	23	121
16–B	Ag_3PO_4	1	240	130	20	21	20	19	17	80

Heat-Resistance of Cured Rubber

The optimum-cured samples described above were heated in carbon dioxide at 100° or 130° C. and the tensile strengths (Fig. 4 and Fig. 5) were determined.

The heat-resistance was increased immensely by addition of silver phosphate, and less so by lead and zinc phosphates. Zinc phosphate had only a slight effect. Magnesium phosphate reduced the heat-resistance. The silver sulfate mixture did not show a definite effect at the temperatures used.

These results are similar to the effect on cure (cf. Ōkita and Hosoya, *J. Soc. Chem. Ind., Japan*, **41**, Suppl. binding, 99–400B (1938)) as well as to the evolution of hydrogen sulfide, as described above.

Conclusion

It is concluded that maximum tensile strength is reached more quickly than normally when the amount of hydrogen sulfide increases above normal. If considerable acid is formed during cure, the amount of hydrogen sulfide evolved decreases, and curing is retarded. The heat-resisting properties are increased by addition of a salt which depresses the amount of hydrogen sulfide evolved. On the contrary, when much strong acid is formed, the deteriorating effect of the acid on the rubber becomes very great and the contrary result is obtained.

[Reprinted from the Journal of the Society of Chemical Industry, Vol. 57, No. 10, pages 327–339, October, 1938.]

Properties and Uses of Chlorinated Rubber

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Although rubber was first chlorinated in 1846 to improve its aging properties (Parks, British patent 11,147), it was not until 1888 that a product containing 65.18 per cent of chlorine was isolated and the formula $C_{10}H_{13}Cl_7$ given by Gladstone and Hibbert.[1] Nearly thirty years later the United Alkali Company marketed a solution of chlorinated rubber, Duroprene, made under the Peachey patents, and for ten years this remained the only chlorinated rubber on the market. During the past ten years interest in this material has rapidly developed, as shown by the numerous brands at present available, namely: Alloprene (I. C. I.); Tornesit (New York Hamburger Gummiwaaren Compagnie, later Chemische Fabrik Buckau); Tegofan (Tegofan Gesellschaft, later Chemische Fabrik Buckau); Pergut (I. G. Farbenindustrie); Detel (Detel Products); Aizen (Hadogaya Soda K. K., Japan); Nippon (Nippon Soda K. K., Japan); Protex (Soc. Ellettrica ed Elettrochimica del Caffaro, Italy); and Dartex (Metallgesellschaft A.-G.).

The patent literature indicates that interest in chlorinated rubber is also taken by Russia, France, Austria, and Jugoslavia.

THE PROPERTIES OF CHLORINATED RUBBER OF PARTICULAR IMPORTANCE TO THE PAINT AND LACQUER INDUSTRY

General Analysis

Chlorinated rubber comes to the consumer as a cream-colored powder, or as a floc-like material. Typical analyses of four marketed brands of chlorinated rubber are shown in Table I.

TABLE I

	A	B	C	D
Apparent chlorine content, per cent	65.0	67.0	66.0	64.5
Ash, per cent	0.2	0.2	0.2	0.6
Insoluble in toluene, per cent	0.3	0.7	0.4	0.3
Moisture content, per cent	0.3	0.3	0.4	0.2
Residual solvent, CCl_4, per cent	5.0	5.5	4.0	8.0
Packing density, grams per liter	370	240	250	380
Dissolution time (toluene), min.	10	10	15	20

The theoretical chlorine content for $C_{10}H_{13}Cl_7$ is 65.13 per cent, but several factors must be taken into account before the figures shown in the table can be strictly compared. The ash from chlorinated rubber usually consists largely of sodium chloride. The moisture content is satisfactorily determined by dissolving the chlorinated rubber in toluene and employing the Dean and Stark apparatus.[2] Residual solvent, determined by the method of Bloomfield, Farmer, and Miller[3] is a characteristic of most brands of solid chlorinated rubber; the solvent is almost certainly present trapped within the cell walls, for on cold-grinding an odorless sample of chlorinated rubber, a slight but definite odor of solvent may be obtained. Extensive research has shown that residual solvent has no deleterious effect on the chemical behavior of the product.

The packing densities given in Table I are representative of the powder type of chlorinated rubber recommended for paint formulations; powders of substantially higher packing density are difficult to produce and, like the flocculent material, which has a packing density of about 70 grams per liter, take longer to dissolve in paint solvents.

The dissolution times shown in Table I represent the time taken to dissolve 40 grams of the sample in 100 cc. of cold toluene on a slowly rotating vertical wheel; the values are therefore only comparative, for by vigorous agitation within the solution, the chlorinated rubber will dissolve completely within two or three minutes.

Solution Viscosity

It is convenient to refer to this property of chlorinated rubber in terms of the absolute viscosity (in poises at 25°) of a solution of 40 grams of the solid in 100 cc. of toluene; measured under these conditions, the marketed brands of chlorinated rubber range in viscosity from about 50 poises down to about 0.5 poise. For practical application in paints and lacquers, where for reasons of economy a high solids-formulation of relatively low viscosity is required, a chlorinated rubber of viscosity about 3 poises is most suitable.

Owing to the wide range of viscosity possible, the different manufacturers have divided their products into arbitrary viscosity grades. Examination of samples shows that the grading adopted conforms approximately to that shown in Table II. The three other brands of chlorinated rubber are also represented in the 1–5 poise range. The extent of variation of viscosity within any given range depends on the manufacturer's system of control.

TABLE II

APPROXIMATE VISCOSITY GRADING

Viscosity (Poises at 25°) of 40 G. in 100 Cc. Toluene	P	Q	R	S	T
Less than 1.0	....	....	.....	..	B
1.0–5.0	Grade B	5–20 sec.	Extra low	N	..
5.0–12	Grade C	....	Low	H	..
12.0–35	Grade D	60 sec.	.....	..	..
35–100	Grade E	200 sec.	Medium	..	..
Over 100	....	400 sec.	High and extra high	..	..

The importance of buying the correct grade of chlorinated rubber is illustrated by the data in Table III obtained on typical samples of two of the grades of Alloprene.

TABLE III

VISCOSITY/CONCENTRATION RELATIONS
ALLOPRENE IN CCl_4

Concn. G./100 G. Soln.	Grade	
	B Poises	D Poises
6.6	0.13	0.4
8.6	0.30	1.2
11.0	0.70	3.4
14.5	2.3	14.7
16.7	4.6	39.9

Note.—These viscosities, in poises at 25°, are typical values only.

The effect of concentration and temperature on the absolute viscosity of solutions of Alloprene is given, within limits, by a general relationship of the type. $n = A \cdot e^{Bc}$ where n = viscosity in poises and c = concentration in weight-per cent, A and B being constants the values of which depend on the temperature and on the solvent employed. Typical figures are given in Table IV.

TABLE IV

Temp. °C.	Alloprene Grade D in CCl_4 — Per Cent Concentration					Alloprene Grade B in Toluene — Per Cent Concentration				
	5.9	8.62	11.1	15.8	20.0	10.4	18.9	25.9	31.7	36.8
15	0.34	1.42	4.6	30.0	155.0	0.07	0.41	1.74	6.43	17.90
25	0.26	1.00	3.0	17.7	99.5	0.06	0.33	1.25	4.70	11.30
35	0.20	0.74	2.1	11.4	51.7	0.05	0.27	0.95	3.35	7.89
45	0.16	0.60	1.5	8.5	36.0	0.04	0.21	0.78	2.42	5.74

When chlorinated rubber is dissolved in a solvent, the solution obtained almost certainly consists of a swollen mass of chloroisoprene units having very varying chain lengths and degrees of mutual interlocking. The viscosity of the solution it a function of the degree of interlocking, the mean chain length of the chloroisoprene unit, and the degree of swelling of the chlorinated rubber by the solvent. Reduction of chain length occurs as chlorination proceeds and it is true to say that, for a series of products produced by the same chlorination, there is a definite relation between the viscosity of the chlorinated rubber and the degree of chlorination. An examination of several hundred samples of independently chlorinated rubber has shown, however, that there is no universal relationship between the viscosity and the chlorine content, the viscosity at any chlorine content being largely governed by the conditions of manufacture; Table V illustrates this point for the final stages of chlorination.

TABLE V

Per Cent Chlorine	Viscosity
63.6	2.33
65.2	1.09
65.4	0.95
65.6	0.82
63.3	1.48
65.2	0.90
66.7	0.56
63.5	0.78
65.3	0.74
65.9	0.67
66.6	0.58

By vigorous treatment it is possible to reduce the viscosity of any sample of chlorinated rubber; for instance, when a 10-per cent solution of grade B Alloprene in carbon tetrachloride is heated for several hours at 140° in an autoclave, the viscosity of the solution is halved; or if a similar solution is left in the dark in the presence of free chlorine, viscosity reduction will occur according to the equation: $\{(\eta_0/\eta_t) - 1\}(1/t) = k$, where η_0 = initial viscosity of the solution, η_t = viscosity after time t, and k is a constant depending on the temperature alone, and independent of the concentration of dissolved chlorine. This reaction has a small temperature coefficient, and an energy of activation of approximately 1000 gram-calories; it has been found that the presence of hydrogen chloride, water, or oxygen does not contribute to the rate of viscosity reduction.

In the presence of light, the same solution containing free chlorine will decrease in viscosity at a greater rate; experiments have shown that photochemical activation of the free chlorine is probably the first step in the process, radiation of the wave-lengths absorbed by chlorine (particularly the band 2800–4100 A. U.), being the most active in promoting viscosity reduction; in the absence of free chlorine, however, this radiation is comparatively ineffective. In the absence of light, as, for instance, in a stored paint, no change in viscosity occurs on storage.

Since the different brands of chlorinated rubber may have been processed under different conditions of viscosity control, brands of the same viscosity may not show

the same relationship between viscosity and the other physical properties normally depending on viscosity.

Properties of Films

Film Formation.—By pouring a solution of chlorinated rubber onto a glass cover slip suspended from a sensitive quartz spring inside a suitable air thermostat, and following the movements of the quartz with a cathetometer, it has been possible to determine the course of evaporation of the solvent from chlorinated rubber under varying conditions of solvent humidity, temperature, and air flow. At 20° a solution of chlorinated rubber in benzene loses solvent at a constant rate until a concentration of about 25 per cent (by weight) is reached; at this concentration the surface tension of the solution, which has been steady at about 30 dynes per cm., increases, and the rate of evaporation of solvent drops to a lower but again constant value. When a concentration of about 60 per cent is reached, the surface tension has reached a value of 43 dynes per cm. and the rate of solvent loss, which has again remained constant, now decreases. Diffusion of solvent through the viscous mass is then the factor governing the rate of film formation, and at a concentration of about 90 per cent the mass is, in fact, a transparent and quite hard film. Removal of the final 10 per cent of solvent is a very slow process, and when only about 3 per cent remains, a brittle and highly transparent film is obtained; if the last traces of solvent are removed, for instance by extracting the film with methyl alcohol, disintegration occurs. A plasticized film is, of course, not brittle in this way. It is of interest to note that the surface tension at 100-per cent concentration, as obtained by extrapolating the reciprocals of the surface tensions at lower concentrations in different solvents, is 175 dynes per cm., being independent both of the solvent used for the determination and of the viscosity of the chlorinated rubber.

Accurate measurements of density have also been made during the course of the evaporation process, and the linear relationship between density and concentration over the earlier stages, followed by a diminution in the density increase during the later stages, suggests strongly that the film as it forms takes up a sponge-like structure and in consequence has a density lower than that of chlorinated rubber when in solution; it is significant that the addition of a suitable plasticizer reduces the rate of passage of water vapor through the film.

Refractive Index Changes.—A large number of measurements have been made of the refractive index of chlorinated rubber at different concentrations in carbon tetrachloride and in toluene, by means of an immersion refractometer fitted with special small-range prisms. The following equation was developed from first principles and found to hold rigidly for solutions of purified chlorinated rubber in both solvents, as it does for mixtures of the solvents themselves:

$$\frac{C(n_{100}^2 - 1)}{100d_{100}(n_{100}^2 + 2)} = \frac{n^2 - 1}{d(n^2 + 2)} - \frac{(100 - C)(n_0^2 - 1)}{100d_0(n_0^2 + 2)}$$

where C = concentration of a solution (wt.-per cent) of refractive index n and density d at 25°, and d_0, n_0, d_{100}, and n_{100} represent the density and refractive index of the solvent and of the solute, respectively.

The importance of this relationship lies in the fact that it has been tested over the lower ranges of concentration where viscosity does not make too difficult the determination of density and refractive index, and since it is known to hold rigidly for mixtures of other and less viscous materials, values for chlorinated rubber deduced from it at higher concentrations have a high probability of being accurate. In this way the refractive index (D line) of solvent-free chlorinated rubber containing 67.4 per cent of combined chlorine was found to be 1.596, being independent of

the solvent used or of the viscosity of the sample; the density was 1.676 at 25°. The ultimate analysis of this sample of purified chlorinated rubber corresponded with the formula $C_{10}H_{13.43}Cl_{7.79}$, indicating a molecular refractivity of 84. This value compares favorably with the calculated value of 83 obtained from the density and refractive index determinations just quoted.

These values for chlorinated rubber may be used for the rapid estimation of the concentration of any solution, provided that the density and refractive index of the solvent itself are known. The calculated density 1.676 also serves as a useful criterion when judging the structure of film, plastic, or molded article. Both refractive index and density depend on the chlorine content of the chlorinated rubber, however, the data in Table VI being the nearest estimate yet made of this

TABLE VI

Unit Formula	Per Cent Chlorine	Density 25°	n_D 25°
$C_{10}H_{14}Cl_6$	61.25	1.585	1.591
$C_{10}H_{12}Cl_7$	65.13	1.641	1.595
$C_{10}H_{12}Cl_8$	68.24	1.691	1.600

variation. The higher refractive index of chlorinated rubber also places it well up in the list of resins, as the values for specular ("mirror-like") reflection in Table VII indicate.[4]

TABLE VII

Resin	n_D 18°	Per Cent Specular Reflection 45°
Bakelite XR 254	1.638	7.20
Coumarone	1.630	7.00
Chlorinated rubber	1.600	6.44
Albertol III L	1.555	6.02
Beckacite 1001	1.552	6.00
Rosin	1.545	5.80
Vinylite	1.475	4.75

Tensile Strength.—It has already been mentioned that the evaporation of a solution of chlorinated rubber in benzene results in a film having a high degree of brittleness. A study has been made of the methods of removing this brittleness and of their effect on the tensile strength of the film. For this work, filtered solutions of chlorinated rubber, in sufficient quantity to produce films approximately 0.001 inch thick, were cast onto glass plates floating on mercury, and the rate of evaporation was controlled by drawing warmed and filtered air over the surface of the solutions for 48 hours; the films so formed were stripped from their glass supports and aged for a further 48 hours at 30–40°; they were then cut into 6 × 1-in. strips and broken on a modified Goodbrand thread-testing machine operating at a rate of traverse of 12 inches per minute; the tensile strengths given below were calculated from twenty tests on each film. The effect of viscosity on the tensile strength of Alloprene is shown in the following figures for strength (lb. per sq. in.) of films containing 20 per cent of dibutyl phthalate: Alloprene grade B, 3100; C, 3000; D, 2700; E, 3100. Thus no marked change is apparent from grades B to E. With Alloprene of still lower viscosity, down to 1 poise, the tensile strength of the plasticized film drops to 800 lb. per sq. in. and for this reason grade B Alloprene is the lowest grade recommended for paint formulations.

The maximum tensile strength of any stable, unplasticized chlorinated rubber appears to be about 6000 lb. per sq. in., but the unplasticized film is brittle. The choice of plasticizer is important since different plasticizers have different effects

on the tensile strength of the film. Thus the average film strength (lb. per sq. in.) of Alloprene (film thickness approximately 0.001 in.) with 25 per cent of the following plasticizers was: dibutyl phthalate, 3300; tricresyl phosphate, 3700; butyl oleate, 1700; amyl stearate, 1600; chlorinated biphenyl, 4700; Cereclor I, 4600. With increasing plasticizer content there is a steady decrease in tensile strength and a corresponding increase in extensibility of the film. The decrease in tensile strength is a minimum when the plasticizer, Cereclor, described later in this paper, is used.

Tested under the same conditions, moisture-proofed Cellophane showed a tensile strength of 9700 lb. per sq. in. and Pliofilm, a strength of 6000 lb. per sq. in. It is clear therefore that while chlorinated rubber has a good film strength it would not compete in this respect with these transparent wrapping materials.

Dielectric Properties of Film.—No significant differences in dielectric properties were found in unplasticized films prepared from four different brands of chlorinated rubber; at a million cycles per second the lowest permittivities (2.4–2.8) were obtained on unplasticized films, which also had the lowest power factors (less than 0.01). Increase of plasticizer content caused a general increase in both the permittivity and the power factor of the films, with a tendency for the volume resistivity (approximately 1×10^{14} ohms per cc.) and breakdown voltage (1000 volts per mil. for a. c.; 5000 for d. c.) to decrease, although the inclusion of plasticizers having low volume resistivity caused no very appreciable reduction in the volume resistivity of the films.

These results indicate that chlorinated rubber lacquers have excellent insulating properties which, in conjunction to their flame and chemical resistance, make them suitable for use in the electrical industry.

Transparency, Photochemical Stability, and Color.—Chlorinated rubber dissolves in many solvents to give solutions of varying degrees of clarity, and the clarity of the solution governs the transparency of the film or lacquer prepared from it.

A chlorinated rubber of high transparency is often desirable. The transparency of a sample of chlorinated rubber may be defined as the amount of visible light passed by a cell 7 mm. long containing a solution of 40 grams of the solid in 100 cc. of toluene, expressed as a percentage of the amount passed by the same length of pure toluene. Typical values are: linseed oil (boiled) 53; tung oil 80; 40 grams of chlorinated rubber in 100 cc. toluene, brand P 44, Q 40, R 49, S 70, T 6 per cent. This test for transparency in toluene is an exceedingly delicate indication of the general purity of a sample of chlorinated rubber; bad color, or a moisture content exceeding about 0.5 per cent due either to bad processing or to storage in a damp atmosphere, will result in the transparency falling from about 70 per cent to below 30–40 per cent.

Similar determinations carried out on films of chlorinated rubber show that the absorption of visible light by a film 0.001 inch thick and plasticized with dibutyl phthalate or with Cereclor is practically negligible, being of the same order as the absorption by such highly transparent materials as Cellophane. Actually about 90 per cent of the intensity of the visible radiation incident on these films passes through, the remainder being lost by the two interfacial reflections that occur. A chlorinated rubber film plasticized with an unsuitable material (for instance, paraffin wax) shows a progressive decrease in transparency with increasing plasticizer content; in the absence of a mutual solvent for instance, 5 per cent of wax reduces the transparency to 60 per cent. Photoelectric determinations of transparency on films may be used therefore for the quantitative examination of the miscibility of resins, waxes, plasticizers, etc., with chlorinated rubber.

With increasing thickness, the transparency of the unplasticized film falls considerably. Thus, for a film thickness of 0.02 mm. the transparency was 90 per cent, 0.08 mm., 88 per cent, and 0.50 mm., 74 per cent. This decrease is due to absorption of radiation at the violet end of the spectrum, a thick film appearing reddish brown by transmitted light.

Comparative determinations of the transparencies of chlorinated rubber and of certain cellulose derivatives to the shortest (ultra-violet) radiation present in sunlight were also carried out on films; the results, shown in Table VIII, indicate that chlorinated rubber might be expected to show sensitivity to strong sunlight comparable with that of cellulose nitrate, and exposure tests on films containing fifty of the commonest plasticizers were accordingly carried out under a carbon arc operating under conditions approximating to strong sunlight during a hot English June and July.

TABLE VIII

FILM TRANSPARENCY IN NEAR ULTRA-VIOLET

Film	Thickness, Mm.	Wave-Length, A. U. 2900	3000	3100	3200
Alloprene, unplasticized	0.030	58	65	69	74
Alloprene with 27 per cent dibutyl phthalate	0.035	1	43	56	65
Cellulose acetate	0.018	52	62	68	72
Cellulose nitrate	0.025	18	33	43	57

The relative increases in color of certain of the films (measured on the Lovibond colorimeter by reflected light) are shown in Table IX, the color increase of the unplasticized chlorinated rubber film being taken as 100. The plasticizers themselves were also compared for ultra-violet absorption and for volatility (relative loss in weight) at 70°.

TABLE IX

PHOTOCHEMICAL STABILIZING ACTION OF PLASTICIZERS

Plasticizer	Relative Color Increase of Film	Log $\frac{\alpha_{2900}}{\alpha_{3100}}$	Volatility 70°
Dimethyl phthalate	39	1.8	90
Diethyl phthalate	46	1.8	73
Butyl stearate	49	0.9	15
Dibutyl phthalate	51	2.3	20
iso-Butyl phthalate	66	1.9	35
Diamyl phthalate	66	2.5	7
Benzyl benzoate	96	1.3	97
Triacetin	102	0.3	700
Butyl oleate	109	0.5	30
Chlorinated biphenyl	149	0.3	nil
Triethyl citrate	156	0.4	57
Amyl lactate	167	0.4	...
Tricresyl phosphate	375	0.6	1

It will be seen from the third column in Table IX that the plasticizers which stabilize best are those of which the ultra-violet absorption increases very selectively on approaching the wave-length 2900 A. U. from the direction of the wave-length 3100 A. U., that is to say, when log $\alpha_{2900}/\alpha_{3100}$ is greater than one. The possession of a sudden strong absorption of radiation of wave-length about 3100 A. U. appears to impart a protective action to the plasticizer, and it has also been found that cutting off radiation of wave-length less than 3100 A. U. by thin glass filters very largely prevents discoloration of the unplasticized film. A chlorinated rubber film containing 20–30 per cent of dibutyl phthalate is as stable to strong sunlight as films of the usual cellulose derivatives, and the use of tricresyl phosphate, or of tartrates,

citrates, and lactates, as plasticizers in unpigmented films exposed to sunlight is strongly to be deprecated. Further tests under strong sunlight entirely confirmed these findings and also showed that aromatic sulfonamides, glyceryl acetates, glyceryl or glycol ethers, and camphor were liable to accelerate rather than retard the rates of discoloration of chlorinated rubber films, and that certain organic peroxides (as disclosed in British patent 432,905) prevented the development of opacity during these tests. The development of acidity by chlorinated rubber due to purely photochemical decomposition will be dealt with in the next section.

In view of the mechanism of the photochemical stabilizing action of plasticizers (see above) it would be expected that the more plasticizer present the greater will be the protective action; that this is actually the case is shown by the data obtained from short-period exposure tests under the carbon arc, a film containing 10 per cent of dibutyl phthalate having a relative color after test of 61, with 20 per cent 42, with 30 per cent 33, and with 40 per cent 28 (relative to 100 for the non-plasticized film); the color of the unexposed film was 17 per cent.

In addition to its transparency, the depth of color of a solution of chlorinated rubber is of commercial importance, since bad or varying color will make difficult the formulation of satisfactory lacquers and may even interfere with the tint of a light-colored paint. Determinations of the color of marketed brands of chlorinated rubber were made on a standard solution of 40 grams of solid in 100 cc. of toluene contained in a 0.75-inch diameter white glass tube placed upright in front of the slot of a B. D. H. Lovibond Tintometer. The sum of the red, yellow, and blue units is taken for convenience as the color index of the chlorinated rubber. Boiled linseed oil had a color index of 50, tung oil 18, chlorinated rubber, brand P 36, Q 32, R 28, S 24, and T 48. It will be seen that there is considerable variation in the color of solutions of the marketed brands of chlorinated rubber.

The color of chlorinated rubber solutions is due to chlorinated rubber resins (soluble in methyl alcohol) and also to the unsaturated decomposition products formed when chlorinated rubber is caused to lose traces of hydrogen chloride by a vigorous treatment such as exposure to strong ultra-violet light, or heating above 140°. The formation of these colored decomposition products is also catalyzed at the higher temperatures by salts of certain metals, notably iron, and possibly also copper, and by strong bases such as ammonia, phenylhydrazine, or caustic soda. The development of this color in chlorinated rubber is by no means an indication that the colored chlorinated rubber is unstable, for one of the most effective methods of thermally stabilizing chlorinated rubber is to heat it in the dry state for several days at 140°, as described in British patent 454,576 (assigned to I. C. I.). That the slightly colored and more stable chlorinated rubber so obtained owes its color to the presence of traces of unsaturated decomposition products is suggested by the fact that if a trace of chlorine is introduced into a solution of this product, the brown color instantly disappears; irradiation in the presence of oxygen, either free or as peroxides, will also remove the color.

It may be concluded that the best brands of chlorinated rubber compare more than favorably in color with many of the common components of paints and lacquers, and that the presence of a slight color is more often than not an indication of good stability; at the same time it will be appreciated that chlorinated rubber is not as suitable for the production of colorless articles as certain of the resins available on the market which have not the outstanding properties of chlorinated rubber in other directions.

Odor.—Many of the solvents and plasticizers for chlorinated rubber have characteristic odors, which are retained to a greater or less extent when these materials are

used in chlorinated rubber films and finishes; this can, of course, be obviated by the correct choice of odorless solvents and plasticizers, and nearly all criticisms of chlorinated rubber in this respect have been traced to the wrong selection of these other components of the finish.

Stability of Chlorinated Rubber

The stability of chlorinated rubber depends on three factors.

Instability due to Free Hydrogen Chloride.—By inadequate processing, a manufacturer may leave in the chlorinated rubber traces of free hydrogen chloride which, although "free" in the sense that it is not combined with the chlorinated rubber, cannot be completely removed by washing the solid with water or dilute alkali. This free acid may result in tendering of paper or cloth or cause corrosion and the development of pressure in the metallic containers used for the storage of chlorinated rubber formulations. A reliable test for this type of instability is to dissolve the sample of chlorinated rubber in an excess of neutralized toluene, thereby breaking down all the cell structures, and then to add this solution to neutral methyl alcohol, shaking well to break up the coagulum; after adding a little distilled water and a few drops of bromophenol blue, the liquid phase may be titrated directly for total acidity.

Samples of chlorinated rubber which, by this test, show any traces of free acidity should not be used for formulating paints or lacquers or for treating cloth, paper, or metals, unless the free acidity is counteracted, for instance by the addition of basic pigments. There are, however, brands of chlorinated rubber available which have no free acidity and are therefore to be preferred. For example, brands P and S have no free acidity, brand T contains 0.019 per cent, Q, 0.050 per cent, and R, 0.056 per cent (as HCl).

The presence of a small quantity of free hydrogen chloride in a large bulk of solvent, as in a lacquer during storage, is sufficient to cause a significant degree of corrosion. To demonstrate the effect of this acidity a very sensitive test was devised. Half-inch discs of mild steel were polished to a high degree on one face, and their reflectivity was measured by means of a photoelectric cell. The discs were then suspended by means of small bar magnets at a fixed height above the surface of xylene solutions of different samples of chlorinated rubber contained in small uncorked specimen tubes and maintained at 25 and 75 per cent humidity in total darkness. The rate of tarnishing of the discs was followed by periodic measurement of the disc reflectivity, and in Table X the reflectivities of the discs are expressed as percentages of their initial reflectivities after various periods of exposure.

TABLE X

Brand	Disc Reflectivities after Exposure for (Hrs.) 0	24	96	360	1000
P	100	100	98	98	98
Q	100	80	66	5	3
R	100	96	91	22	8
S	100	99	94	92	91

A broad correlation was also found between the free acidity of a sample of chlorinated rubber and the rate of tarnishing of the corresponding disc. This test, inasmuch as it measures the effect of a catalyst (the tarnishing is, of course, due to the formation of iron hydroxides, catalyzed by the acid), is an extremely sensitive indication of the presence of that catalyst, and can be recommended for trial with any chlorinated organic material suspected of instability, under different conditions of temperature, humidity, and light.

It is clear, therefore, that the elimination of free acidity is essential to the production of a reliable chlorinated rubber.

Photochemical Instability.—The second type of instability possible with chlorinated rubber is that due to photochemical decomposition, already partly described in the section dealing with color and transparency. Under the conditions detailed in that section, it is possible to obtain hydrogen chloride at room temperature from a sample of chlorinated rubber which is completely neutral by the test of free acidity. To demonstrate this, solid chlorinated rubber was irradiated in quartz tubes under a quartz mercury-vapor lamp (emitting radiation down to 1800 A. U.), gaseous products being swept away continuously by a stream of nitrogen into Drechsel bottles containing distilled water. The total energy incident upon each square centimeter of chlorinated rubber was determined by means of the uranyl oxalate radiometer described by Anderson and Robinson,[5] and the contents of the bottles were titrated electrometrically against standard silver nitrate solution, with the results shown in Table XI.

TABLE XI

Material Irradiated	U. V. Energy per Sq. Cm. (Ergs)	Wt.-Per Cent HCl
Commercial chlorinated rubber	42.5×10^8	0.161
Commercial chlorinated rubber after MeOH treatment	42.5×10^8	0.108
With 5 per cent glycidyl phenyl ether	42.5×10^8	0.006
First sample shielded from rays	33.9×10^8	0.003

Photochemical instability is, therefore, only partly due to the presence of residual solvent or resinous impurities in the chlorinated rubber, since exhaustive treatment with methyl alcohol does not remove the instability; moreover, as might be expected, an acid-acceptor of the ethylene oxide type covered by I. G. in British patent 418,230 will also prevent the evolution of hydrogen chloride in the cold during vigorous ultra-violet irradiation. Such an acid-acceptor only masks the decomposition of the chlorinated rubber, however, and consequently it is preferable to prevent photochemical decomposition occurring either by not exposing the chlorinated rubber to the direct rays of the strongest sunlight (diffused daylight alone is not sufficiently powerful to be of importance), or else to add to the chlorinated rubber an ultra-violet filter of the dibutyl phthalate type; or, as in a paint formulation, to add pigments themselves capable of absorbing and reflecting the harmful radiation.

Thermal Instability.—The third type of instability possible in chlorinated rubber is that due to thermal decomposition of the molecule. This decomposition can occur in complete darkness in a sample of chlorinated rubber which by exhaustive precipitation with methyl alcohol has been purified from residual solvent, such as carbon tetrachloride and chlorinated rubber resins.

In the development of Alloprene, the following thermal stability test has been standardized. Five grams of solid chlorinated rubber, loosely packed in an upright glass tube, are immersed in an oil bath maintained at 130° and evolved gases are carried off continuously, by means of a stream of dry nitrogen entering at the base of the tube, into Drechsel bottles containing distilled water. Periodic electrometric titrations of the contents of these bottles enable the course of evolution of hydrogen chloride to be followed; each test is continued for a minimum of fifty hours, and certain tests are extended to 500 hours. The results of these tests, considered in conjunction with the free acidity titrations carried out on the solid in the manner already described, have enabled a number of important conclusions to be drawn regarding the purely thermal decomposition of chlorinated rubber.

Effect of Degree of Chlorination on Thermal Stability.—The literature reveals that incompletely chlorinated rubber has poor stability, correct statements of the most desirable degrees of chlorination having been made in several papers and in numerous patents; there is nothing novel, therefore, in the conclusion that the higher is the degree of chlorination the greater is the stability of the chlorinated rubber. It may be of interest, however, to give the results of thermal stability measurements carried out at 130° on a total of 333 samples of chlorinated rubber, the true chlorine contents of which have also been determined; these chlorine contents, corrected for residual solvent, are shown in column one of Table XII, from which the probable decomposition pressure of samples of solid chlorinated rubber having chlorine contents corresponding with certain theoretical stages in chlorination may be estimated.

TABLE XII

Chlorine Content, Per Cent	Stage	No. of Samples	Mean Wt. of HCl Evolved in 50 Hrs. at 130°		Probable Variation	
24		1	16.60		.....	
25 (34)	$C_{10}H_{14}Cl_2$	1	15.90	(10.38)	.....	
54 (51.4)	$C_{10}H_{14}Cl_4$	1	3.08	(3.80)	.....	
55		1	2.23		.....	
56		1	2.41		.....	
61 (61.35)	$C_{10}H_{14}Cl_6$	2	1.19	(1.09)	0.67	(0.06)
62		10	0.92		0.62	
63		25	0.74		0.24	
64		63	0.47		0.16	
65 (65.11)	$C_{10}H_{13}Cl_7$	78	0.33	(0.32)	0.08	(0.07)
66		67	0.31		0.07	
67		45	0.29		0.07	(0.06)
68 (68.24)	$C_{10}H_{12}Cl_8$	20	0.29	(0.29)	0.05	
69		10	0.29		0.07	
70 (70.7)	$C_{10}H_{11}Cl_9$	3	0.26	(0.31)	0.03	(0.05)
71		5	0.39		0.16	

The probable variation of the decomposition has been calculated by the law of least squares, and represents the probable variation of any single determination from the mean values given in column three of Table XII. These variations are an interesting indication of the chemical inhomogeneity of the lower chlorinated products, and also indicate the increasing homogeneity of the higher products. These experiments have been repeated 27 more samples of chlorinated rubber freed from resin and residual solvent by precipitation of their solutions into hot methyl alcohol; the same general relationship between degree of chlorination and thermal stability was obtained. The removal of these impurities, however, brought about a reduction of approximately 0.15 in the total weight-per cent of hydrogen chloride evolved in fifty hours at 130°, the reduction being independent of the chlorine content of the chlorinated rubber over the range 63–70 per cent chlorine. It was also found that the addition of carbon tetrachloride to the products had no effect on their stability, indicating that the roughly constant percentage of chlorinated resins was responsible for this 0.15 per cent of acid.

The importance of the degree of chlorination on thermal stability having been established, a large number of chlorinations were carried out at temperatures ranging from 20° to 70° in complete darkness and in quartz apparatus under direct radiation from a quartz mercury-vapor lamp; after fifty-three chlorinations it was concluded that if chlorination was carried to completion, the stability of the product was quite uninfluenced by these variations in the conditions of the chlorination. Chlorination at a higher temperature, the presence of ultra-violet light, or the use of catalysts such as iodine, or the chlorides of nickel, copper, or phosphorus, or the addition of up to 1 per cent of water to the solvent, while in some cases affecting the

rate of chlorination, had no effect on the actual decomposition pressure of the fully chlorinated products. It is concluded from these results that there is no justification for the claims made in the earlier literature that the conditions of the chlorination are highly critical if a chlorinated rubber of good stability is to be obtained; it is considered that the absence of a specific test for thermal instability and failure to take into consideration the degrees of chlorination of the samples have contributed very largely to this impression.

The thermal stabilities of unstabilized marketed brands of chlorinated rubber are as follows (recorded as weight-per cent HCl evolved at 130°/50 hr.): brand P 0.35, Q 0.53, R 0.80, S 0.44; it will be seen that there is very little to choose between them, considering the high temperature and length of the stability test.

The chemistry of the chlorination of rubber has been discussed in considerable detail, particularly by McGavack,[6] Pummerer,[7] Nielsen,[8] Frydlender,[9] Kirchhof,[10] and Baxter.[11] The mechanism of the chlorination is generally agreed to comprise first the substitution of two atoms of chlorine in the $C_{10}H_{16}$ nucleus, and then as a distinct stage the addition of four atoms, and the substitution of one atom of chlorine, resulting in a product of unit formula $C_{10}H_{13}Cl_7$; reference to Table XII will show that products corresponding with this latter mean chlorine content have a minimum thermal instability, and it appears probable in view of the instability of products corresponding in chlorine content with $C_{10}H_{14}Cl_6$, and the relative stability corresponding with $C_{10}H_{12}Cl_8$, that chlorinated rubber having a chlorine content of 65 per cent or slightly higher consists principally of $C_{10}H_{13}Cl_7$ units with more or less of the octachloride, and not of $C_{10}H_{14}Cl_6$ units with more or less of the octachloride, as suggested by Kirchhof.

It is also clear from Table XII that a stable chlorinated rubber having a higher chlorine content than corresponds with an octachloride unit can exist, although this has been denied by other workers; in view of the sharp decrease in viscosity that accompanies the chlorination, it is tentatively suggested that addition of chlorine with some chain rupture is taking place at this stage, resulting in the formation of a number of $C_{10}H_{12}Cl_9$ units; measurements of the evolution of hydrogen chloride and of the total change in chlorine content of the chlorinated rubber have been made and the results support this view. Since, however, the chlorination reaction at this stage is extremely slow and requires ultra-violet radiation for its promotion, these very highly chlorinated products are unlikely to be of more than academic interest.

Variation of Stability with Temperature.—Since the stability of chlorinated rubber is at a maximum and also practically constant, provided that the combined chlorine content of the product lies within the range 65–70 per cent, it is of interest to determine the variation of this stability with temperature; the data in Table XIII represent the weight-per cent of hydrogen chloride evolved during the standard test, by a neutral and slightly underchlorinated product, over the temperature range 70–170°; a kinetic analysis of these data suggests that the decomposition of solid chlorinated rubber is a bimolecular reaction having an energy of activation of approximately 25,000 gram-calories, and the decomposition is probably therefore condensation between two molecular aggregates to form a colored, and slightly unsaturated, but more stable product.

TABLE XIII

VARIATION OF STABILITY WITH TEMPERATURE (ALLOPRENE)

Wt.-Per Cent HCl Evolved during	Temperature					
	70°	70–110°	110–130°	130–140°	140–150°	170°
0–24 hrs.	0.001	0.018	0.235	0.64	1.28	4.90
0–48 hrs.	0.003	0.045	0.405	1.42	2.06	8.11

Advantage of this enhanced stability is taken by I. C. I. (British patent 454,576), claiming a process for the production of a stable chlorinated rubber by subjecting the fully chlorinated material to a temperature of 110–145° (preferably 130–140°) for at least 24 hours; in an example cited in the patent, a chlorinated rubber which had 66.3 per cent combined chlorine content and had been so treated evolved only 0.06 per cent of hydrogen chloride, instead of the original 0.31 per cent, on testing for stability under the standard conditions. If this heat-maturing process is carried too far, or if catalysts are present, the condensation product becomes insoluble in the usual chlorinated rubber solvents.

Flame-Resistance.—In the absence of oxygen, chlorinated rubber submitted to higher temperatures (*e. g.*, 230–300°) evolves copious fumes of hydrogen chloride and leaves a charred residue. In excess of air at 230–280° the products of combustion were found to be 55 per cent of hydrogen chloride, 12 per cent of carbonaceous residue containing 12 per cent of ash and 11.3 per cent of combined chlorine, and 33 per cent of volatile hydrocarbons and esters containing 33 per cent of chlorine and some oxygen. The temperature at which chlorinated rubber will ignite in a flame is of the same order as that of Cellophane,[12] but the very copious evolution of hydrogen chloride which occurs immediately smothers not only the chlorinated rubber but any surrounding conflagration. Chlorinated rubber is, therefore, of considerable value as a lacquer ingredient which at the same time is a fire-extinguisher. Dawson,[13] for instance, finds it very effective in causing the rapid extinction of flame when compounded with inflammable rubber mixes. In addition, there is no danger of the products of combustion causing suffocation or poisoning unawares, since the acid fumes given off by burning chlorinated rubber are an efficient warning agent.

Addition of Stabilizers to Chlorinated Rubber.—It has been shown that chlorinated rubber, correctly prepared, is completely stable up to 100°; it is not recommended for use in paints to be submitted to temperatures higher than that, and in the presence of liquids, a maximum temperature of about 60° represents a reasonable margin of safety. With these reservations, there is no doubt that chlorinated rubber is a completely stable and highly resistant material. Although many stabilizers have been proposed, notable ones being the I. G. ethylene oxide derivatives (British patent 418,230), the alkali salts of hydrocyanic acid or of fatty acids (Deuts. Gold- u. Silberscheideanstalt, British patent 438,843), and esters of polyhydric alcohols containing at least one free hydroxyl group (I. C. I., British patent application 16,915/1936), the use of these materials is of very limited value, since for ordinary purposes chlorinated rubber needs no stabilizer, and at the highest temperatures a stabilizer, if effective in absorbing hydrogen chloride, becomes saturated and therefore inoperative in a definite time, depending on the quantity present. Moreover, a stabilizer which acts as an acid-acceptor does not prevent the chlorinated rubber from decomposing, with the consequent development of color, insoluble matter, and general disintegration of the film; it is clearly most preferable to realize the conditions under which chlorinated rubber can properly be used, and to restrict the use of the material to those conditions, when the use of a temporary stabilizer will be unnecessary.

Relation of Thermal Stability to Other Factors.—The thermal stability of chlorinated rubber is a direct measure of the degree of chlorination of the isoprene unit, and is therefore connected with properties such as refractive index and absolute density; it is not directly connected therefore with viscosity, which depends primarily on the degree of physical complexity of the rubber. A sample of chlorinated rubber of high viscosity may, therefore, be more unstable than one of low viscosity, since manufacturers may produce products of higher viscosity by not taking the

chlorination to completion. If it is necessary to use products of higher viscosity for any purpose in which stability is of first importance, the stability of the high-viscosity material should be checked by the method described.

Chemical Resistance of Chlorinated Rubber

The resistance of chlorinated rubber to hot and cold acids and alkalies has been determined by a method likely to approximate in conditions to those obtaining when chlorinated rubber paints are tested, namely, in film form. The changes in tensile strength and in weight of the film are recorded for several reagents in Table XIV.

TABLE XIV

CHEMICAL RESISTANCE OF CHLORINATED RUBBER

Chlorinated Rubber Film 0.026 Mm. Thick, Containing 4 Per Cent of Residual Toluene

Temp. ° C.	Reagent	Concn.	Duration of Test, Hrs.	Change in Wt.- Per Cent	Tensile Strength, Lb. per Sq. In. Before	After
20	NaOH	100 grams per l.	168	nil	5800	5900
		300 grams per l.	168	nil	5800	5800
		600 grams per l.	168	nil	5800	6000
	Aq. NH_3	0.880	168	nil	5400	6000
	HNO_3	concd.	168	+2.3	5400	5900
	HCl	concd.	168	nil	6500	5200
	NaOCl	5 per cent av. Cl	48	nil	5500	4700
		15 per cent av. Cl	48	nil	5500	4400
	NaCl	10 per cent satd.	48	nil	5500	5500
			48	nil	5500	5200
	Acetic acid	glacial	168	+3.0	5400	4000
	Formic acid	concd.	168	+3.0	5400	4700
	Petrol	.....	168	nil	5700	4600
40	Petrol	.....	48	nil	5650	2500
	Water	.....	48	nil	5700	4900
	NaOH	100 grams per l.	48	nil	6500	4900
		300 grams per l.	48	nil	6500	4600
		600 grams per l.	48	nil	6500	5500
60	HCl	10 per cent concd.	48	nil	5500	5300
			48	nil	5600	3700
	NaOCl	5 per cent av. Cl	48	nil	4800	4100
		15 per cent av. Cl	48	nil	4800	3200
	NaCl	10 per cent satd.	48	nil	4800	4500
			48	nil	4800	4500

The change in tensile strength is a more important and more sensitive test of attack than the change in mass, and these figures, while by no means complete, demonstrate the remarkable resistance of chlorinated rubber to acids and alkalies at temperatures of 40° and under. The action of light petroleum at 40° is due to the removal of residual solvent from these unplasticized films; similarly, it is probable that where the other reagents have had a slight effect on the tensile strength of the film it has been due to attack on the solvent rather than on the chlorinated rubber. Slight variations in the residual solvent content are responsible also for the variation in tensile strength of the films before the test.

Tests in which solid chlorinated rubber was immersed for several weeks at 40° in aqueous caustic soda, hydrochloric, nitric, acetic, and formic acids both concentrated and dilute, confirmed the tests on films, and a very high resistance was also found to attack by gaseous chlorine, ammonia, sulfur dioxide, and hydrofluoric acid.

APPLICATIONS OF CHLORINATED RUBBER

Choice of Plasticizer

It has already been shown that chlorinated rubber requires plasticizing to reduce the brittleness of its films, and in the choice of a plasticizer lies the possibility of making or marring the protective qualities of a chlorinated rubber finish. The inclusion in a formulation of a readily saponifiable plasticizer, for instance of the ester type, will, of course, make the finish so obtained quite susceptible to alkali, and in the past there is no doubt that the chlorinated rubber itself has been blamed for the failure which must occur in these cases.

The necessity for developing chemically resistant plasticizers has been appreciated by several manufacturers, and among the plasticizers now recommended for use with chlorinated rubber are sulfurized terpenes (U. S. patent 2,046,277), hydrogenated abietic esters such as Hercolyn, sulfurized tung oil (U. S. patent 2,068,818), chlorinated diphenyl (U. S. patent 1,950,894 and 2,044,505), "T" oil (a non-volatile sulfur–toluene condensation product manufactured by the I. G. (British patent 429,764), alkylnaphthalenes (I. G., British patent 438,441 and 440,371), chlorinated drying oils (Dunlop Rubber Co., British patent 420,116), and the I. C. I. plasticizer Cereclor.

Cereclor.—Cereclor is a viscous, yellow liquid distinguished by its non-volatility, high solubility in chlorinated rubber solvents, resistance to chemicals, and absence of marked odor; it is prepared in two grades of viscosity, the higher of which (Cereclor I) is generally used for plasticizing chlorinated rubber. Cereclor I contains 47 per cent Cl and has d^{25} 1.23, and viscosity 230 poises at 25°, while Cereclor II contains 42 per cent Cl and has $d^{25.5}$ 1.16, viscosity 25 poises. Both have vapor pressures less than 10^{-5} mm. Hg at 170°. Cereclor has a high resistance to aqueous boiling caustic soda, to sulfuric, nitric, and hydrochloric acids, and is insoluble in water; its thermal stability is comparable with that of chlorinated rubber. It is miscible with chlorinated rubber in all proportions, yielding a series of plastics varying in consistency from sticky, viscous liquids to hard film-forming solids, the properties of which will be discussed later.

In general, chlorinated rubber plasticized with Cereclor will be resistant when cold to most chemicals or combinations of chemicals other than the organic liquids in which chlorinated rubber and Cereclor are soluble; as the temperature of the test is raised from 40° to 60° a slight breakdown may be noticeable in the presence of concentrated sulfuric acid, but in general the chemical resistance is well maintained.

Paint and Lacquer Formulations Based on Chlorinated Rubber

It is not proposed in this paper to give detailed formulations for paints and lacquers, but rather to indicate general principles.

Solvent.—An advantage of chlorinated rubber is that it is very soluble in the cheap solvents; a full list of solvents and non-solvents has been prepared by Kolke.[14] Alloprene is soluble in, or miscible with, benzene, chlorobenzene, toluene, solvent naphtha, decalin, tetralin, trichloroethylene, carbon tetrachloride, tetrachloroethane, diacetone alcohol, furfuraldehyde, ethyl and *n*-butyl acetate, methylethyl ketone, cyclohexanone, triacetin, tricresyl phosphate, butyl oleate and phthalate, Cereclor I, linseed oil, Seekay wax, coumarone resin, shellac, cellulose nitrate and acetate, and dammar gum. In general, xylene is the best solvent for paint work, with the addition of decalin and solvent naphtha (aromatic), according to the rate of drying required; these solvents should be free from high-boiling impurities which would tend to leave a soft or strong-smelling film.

Plasticizer.—For chemically resistant formulations the use of a chemically resistant plasticizer is advised; in the absence of corrosive conditions and where maximum resistance to sunlight is required, dibutyl or diamyl phthalate may be used; for decorative finishes where chemical resistance is not of primary importance, boiled linseed oil or heat-treated China wood oil will give very satisfactory results. If other plasticizers are used, it must be established that they are completely miscible with chlorinated rubber, otherwise a brittle film will result.

TABLE XV

MOISTURE-PERMEABILITY OF CHLORINATED RUBBER FILM

Film	Thickness, Mm.	Mg. per Hr. per Sq. In.
100 per cent chlorinated rubber	0.034	0.30
75 per cent chlorinated rubber, 25 per cent dibutyl phthalate	0.025	0.70
75 per cent chlorinated rubber, 25 per cent tricresyl phosphate	0.029	0.19
75 per cent chlorinated rubber, 25 per cent butyl oleate	0.034	0.65
75 per cent chlorinated rubber, 25 per cent amyl stearate	0.024	1.06
75 per cent chlorinated rubber, 25 per cent chlorodiphenyl	0.028	0.12
75 per cent chlorinated rubber, 25 per cent Cereclor I	0.027	0.16
Viscose film standard	0.024	4.22
Viscose film moistureproofed	0.028	0.36
Rubber hydrochloride	0.024	0.23
Cellulose acetate	0.020	3.29
Benzylcellulose	0.036	1.57
Transparent wrapping paper	0.019	3.76
Parchmentized wrapping paper	0.093	4.06

Resin.—Various compatible resins may be incorporated.

Pigments.—Most pigments can be used, and in all cases the pigment must be quite dry before incorporation. Lithopone and white lead for wood primers, red lead for metal primers, and zinc oxide and titanium oxide for finishing coats, are satisfactory; inert pigments such as silica are claimed to promote mechanical resistance in the paint film.

Formulation of Chlorinated Rubber Finishes.—For finishes required to resist a high degree of chemical attack, a formulation based on 60 Alloprene : 40 Cereclor is highly satisfactory; for less stringent conditions, part of the Alloprene may be replaced by a suitable resin.

Applications of Chlorinated Rubber for Moistureproofing

Since rubber itself is used for moistureproofing a wide variety of materials, it is natural to investigate the use of chlorinated rubber for this purpose, particularly where the additional properties (flame-resistance, chemical resistance, etc.) of the chlorinated derivative would be advantageous. Before considering the properties of materials so treated, an examination was made of the relative rates of passage of water vapor through detached films of chlorinated rubber and of various cellulose derivatives. Discs of the film under examination were placed over the ground end of a closed glass tube carrying a weighed quantity of calcium chloride; the tubes thus sealed were placed in an air thermostat at 25° and a humidity of 79 per cent was maintained around them by means of an ammonium chloride control. Periodic determinations of the weight of the calcium chloride containers made over a period of 14 days established that under these conditions the rate of passage of water vapor through the films became constant at the end of the first day. The results in Table XV represent the mean of duplicate determinations continued for seven days under the test conditions.

They indicate the remarkable impermeability of unplasticized and of correctly plasticized chlorinated rubber film to water vapor; in further tests on films containing 25 per cent of Cereclor, it was also found that the permeability per unit thickness decreased very rapidly as the thickness of the film increased from 0.13 to 0.35 mm.

Additional data from direct contact tests under a head of 5 cm. of water showed that no trace of water was passed during 7 days at 22° by the unplasticized film and by films plasticized with Cereclor, dibutyl phthalate, and tricresyl phosphate, although the other chlorinated rubber films and the films of cellulose derivatives passed definite, though in some cases only very small, quantities of water. In addition to indicating the high degree of water-impermeability which may be expected from chlorinated rubber paints and lacquers, these results will be of considerable interest to the manufacturer of moistureproofed materials. Use has already been made of this property, *e. g.*, for moistureproofing transparent viscose wrapping materials (British patent 447,371 and 410,534) and for impregnating cloth (British patent 464,280 and 418,976).

There is a danger in the use of incorrectly processed chlorinated rubber in conjunction with cellulose, since traces of hydrogen chloride liberated by the chlorinated rubber may cause chemical tendering. An investigation was therefore made of the relative rates of tendering of a light cotton cloth treated with chlorinated rubber solution, and with solutions of other impregnants, during exposure to the carbon arc. The cloths were impregnated by dipping in 2 per cent benzene solution and draining off excess of solution, and their rates of tendering were estimated by the cuprammonium hydroxide fluidity method of Clibbens and Ridge and their coworkers.[15] The results of Table XVI demonstrate that a stable type of chlorinated rubber such as Alloprene, even when present to the extent of 5 per cent on a very light cotton cloth during exposure to the carbon arc, causes only the slightest increase in the rate of tendering.

TABLE XVI

Impregnant	Wt.-Per Cent on Cloth	Relative Strength after (Hrs.) 24	48	96
None (benzene only)	..	90	84	73
Alloprene	5.6	85	77	68
Alloprene + 30 per cent dibutyl phthalate	7.8	90	84	74
Alloprene + 60 per cent red lead	21.7	88	81	70
Paraffin wax	9.0	90	84	76
Latex emulsion	6.9	91	85	80

Inclusion of the photochemical stabilizer dibutyl phthalate stops completely any tendency of the chlorinated rubber to accelerate the tendering normally occuring in the cloth. On heavy cloths such as calico, tests of this type were unable to detect any tendering during 96 hours' exposure to the carbon arc.

The high gloss, flexibility, and moisture-resistance of chlorinated rubber paints and lacquers make them suitable for finishing decorative papers for magazine covers, book wrappers, and general packages.

In general it is not possible to flameproof paper or cloth with chlorinated rubber without overloading, and it is preferable therefore to incorporate a fireproofing salt in the material, and then to waterproof the fireproofed article, by coating with a plasticized chlorinated rubber lacquer in a non-inflammable solvent. In this way it is possible to obtain flexible fabrics having a good degree of flame-resistance and at the same time exhibiting the chemical and moisture resistance of chlorinated rubber.

Plastic Masses from Chlorinated Rubber

Preparation.—Plasticized chlorinated rubber has also a variety of uses in the massive form. This may readily be prepared, for instance, by gradually adding powder Alloprene to Cereclor I at a temperature of 90–100° in a steam-heated mixer of the Werner Pfleiderer type. After thorough mixing, the charge may be transferred to steam-heated rolls for the addition of fillers, pigments, etc., as in the compounding of rubber mixes. The resulting plastic masses have been considered for a large variety of uses, ranging from the manufacture of linoleum to the lining of tanks and the sealing of pipe lines; they may be applied either by warming until sufficiently soft, or by treating with solvent which can later be allowed to evaporate. In view of the wide miscibility of chlorinated rubber with many materials the number of plastics preparable in this way is very great: compositions containing Seekay wax (I. C. I. chlorinated naphthalene) or Cereclor I are of special interest, their resistance to corrosive chemicals being comparable with that of Alloprene itself, and a study has been made of the systems Alloprene–Cereclor and Alloprene–Seekay wax in some detail. The former system comprises plastics ranging from sticky semi-fluid masses, through highly elastic masses to tough inelastic but plastic compositions. The latter system comprises chiefly a range of hard and somewhat brittle plastics of considerably higher softening temperature.

Properties.—Table XVII illustrates the variation of density with composition for the two sets of plastics over a temperature range 18–70°.

TABLE XVII

	Density, Grams per Cc.	
	18°	70°
Per Cent Alloprene–Seekay Wax		
0	1.582	1.572
5	1.567	1.555
10	1.548	1.546
40	1.577	1.605
80	1.615	1.636
90	1.623	1.639
100	1.632	...
Per Cent Alloprene–Cereclor I		
0	1.235	1.232
40	1.387	1.400
50	1.420	1.435
100	1.632	...

Table XVIII indicates the variation of softening point (as determined by the B. S. S. ring and ball test) with composition, two grades of Seekay wax of different setting point being used in the mixes.

TABLE XVIII

Grade B	Softening Temperature, ° C.		
Per Cent Alloprene	Cereclor I	R. 93	R. 123
0	−25	91	123
5	..	88	..
10	..	86	120
30	63	89	119
40	80	91	..
50	99	95	122

By direct mixing it is not easy to obtain plastics containing more than about 60 per cent of chlorinated rubber, since above this concentration the softening point of the plastic approaches too close to the decomposition temperature of chlorinated rubber to allow mixing to be carried on; the density determinations shown in Table

XVII were, therefore, obtained by extrapolating the densities of solutions of the plastics of increasing concentration.

Some idea of the plasticity of these mixes can be obtained from Table XIX, which shows their rates of flow under the ring and ball test, at various temperatures near to the softening point of the plastics.

TABLE XIX

Wt.-Per Cent Alloprene	Rate of Flow (Cm. per Min.) Cereclor I 55°	Seekay Wax R. 93 77°	Seekay Wax R. 93 80°
5	...	0.025	...
10	...	0.048	...
30	1.27	0.040	0.195
40	0.25	0.020	0.105
50	0.075	0.010	0.070

It has been found that the viscosities of toluene solutions of these plastics are practically identical with the viscosities of toluene solutions of the same amounts of Alloprene.

The color of the plastics may be of importance in certain applications. Tests have indicated that the color, measured in the standard toluene solution, is usually rather darker for the plastic than for the individual components, due to the mixing operation, which is conducted at 100°.

The color of these plastics is, of course, liable to vary from a creamy white to a marked brown; if a black Seekay wax is used as a component, the resulting plastic will be dark brown or black. The color can be controlled over a wide range.

The variation of the dielectric properties of Alloprene–Seekay wax plastics is shown in Table XX; similar determinations for the Alloprene–Cereclor system were not carried out, due to the softness of these products.

TABLE XX

Per Cent Alloprene	Permittivity, 50 Cycles/Sec. at 22°	Power Factor, 50 Cycles/Sec. at 22°
0	5.1	0.0020
30	4.4	0.0062
40	4.0	0.0084
50	3.9	0.0092
100	3.0	0.0100

Volume resistivity 10^{15}–10^{16} ohms/cm.^{3} throughout.

The properties of all these plastics may be further modified by the addition of fillers such as cork dust, kieselguhr, wood meal, asbestos fiber, chalk, mica, slate dust, silica, etc., or pigments such as the iron oxides or aluminum powder; the range of products so obtainable is clearly very wide, and it is true to say that the possibilities of these materials have not yet been fully realized.

Uses.—Uses for which these plastic masses have already been suggested include tank linings and pipe-jointing compounds (British patent 450,683), rubber plastics (see British patent 446,278), and non-inflammable dielectrics (British patent 438,807 and 445,710). Containers of metal, wood, fiber, etc., have been sealed very successfully with a variety of these plastics.

The substitution of Alloprene–Cereclor plastics for the linseed oil base used in the manufacture of linoleum leads to an improvement in flame-resistance and in resistance to dilute alkalies, such as washing soda; chlorinated rubber linoleum, being of improved chemical resistance, may be used for covering surfaces other than floors, such as benches, table-tops, walls, etc. The preparation of chlorinated rubber linoplastic and of floor coverings therefrom is fully described (cf. British patents 424,335, 443,585, 443,654, and 456,829).

In addition to the incorporation of chlorinated rubber with plasticizers such as Cereclor and Seekay wax, the addition of chlorinated rubber to putty,[16] to phenol–formaldehyde resins (Dunlop, Canadian patent 355,483), and to tars may be mentioned. The incorporation of chlorinated rubber in low-temperature, coke-oven, and horizontal- and vertical-retort tars has been investigated by the D. S. I. R.[17]; it was found that chlorinated rubber was not readily compatible with low-temperature tars, but yielded stable and often elastic masses with other tars. J. R. Geigy A.-G. has also taken out a patent (British patent 434,159) for the improvement of the viscosity of vertical-retort tars by the incorporation of chlorinated rubber.

Chlorinated Rubber Adhesive

Adhesives for wood, metal, fabrics, paper, cement, etc., have been prepared from chlorinated rubber plastics, either with or without the addition of solvent such as benzene or toluene. Adhesive tape for electrical work and sticky bands for trapping insects either indoors or on trees have also been prepared. In addition, the aqueous chlorinated rubber emulsions, described later for the preparation of porous blocks, may be used as adhesives. On account of the necessarily higher price of these adhesives, their use will be restricted to special applications where high water resistance, fungus resistance, or chemical resistance is required.

Chlorinated Rubber for Sound and Heat Insulation

Apart from the loose fibrous form of chlorinated rubber already referred to, which may be used for general insulation purposes, a special form of chlorinated rubber has been developed which overcomes any tendency of the fibrous form when loosely packed to settle down. This form of chlorinated rubber, known as the porous block, is produced according to British patent 416,056; powdered chlorinated rubber is dissolved in a solvent such as carbon tetrachloride, to give solutions of 10–15-per cent concentration, which are then emulsified with an equal volume of water containing a suitable emulsifying agent; plasticizers or dyes may be added to the chlorinated rubber solution before emulsification, according to the type of porous block required. The emulsion is then injected into a suitable mold consisting generally of a narrow steam-jacketed chamber. By the application of heat the solvent is removed, leaving a wet porous block which is then dried in an air oven, and which has a uniform porosity and an apparent density of 50–100 grams per liter. The block may be reinforced both internally and externally by wires, tubes, or sheets of paper, card, metal, or wood (British patent 427,815); the blocks may be cemented together, preferably by using a small quantity of the original emulsion as the cementing medium; they may also be finished by painting with chlorinated rubber emulsion, lacquer, or paint.

TABLE XXI

Material	Bulk Density, Grams per L.	Thermal Conductivity, Grams-cal. per Cm. per Sec. per ° C.	Mean Temp., ° C.
Alloprene powder	390	0.97×10^{-4}	70
Alloprene fiber	140	0.84×10^{-4}	70
Alloprene porous block	90	1.28×10^{-4}	50
Cork block	180	1.38×10^{-4}	50
Cork, granulated	130	1.12×10^{-4}	70
Cotton wool	80	1.55×10^{-4}	70
Magnesium oxide	170	1.39×10^{-4}	70
Magnesia asbestos	170	1.51×10^{-4}	70
Glass wool	130	1.20×10^{-4}	70

Forms of solid chlorinated rubber intermediate between the fibrous variety and the porous block may also be obtained by agitating the fiber in water and pressing

out the resulting pulp into a paper or hard sheet, according to the pressure applied. These products are, of course, quite distinct from the expanded form of chlorinated rubber described by Redfarn and Schidrowitz (British patent 424,561).

Measurements of the thermal conductivity of Alloprene in various forms are recorded in Table XXI.

Chlorinated rubber as a heat-insulator must not be used at temperatures above 100°, however, on account of the risk of thermal decomposition. It is suitable for the insulation of refrigerators of all types, including those used by ships and railway wagons carrying fruit, or for ice-cream containers or domestic models.

An important advantage of chlorinated rubber for sound or heat insulation is that it absorbs minimum amounts of water even in highly humid atmospheres; when stored for six days in an atmosphere saturated with water at 35°, Alloprene was found to absorb less than one-tenth the weight of water absorbed under the same conditions by a soundproofing material based on cellulose; this property is of importance in the insulation of air-borne craft where dead weight must be reduced to a minimum.

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REFERENCES

[1] *J. Chem. Soc.*, **53**, 679 (1888). For early literature see J. J. Berzelius, "Lehrbuch der Chemie, (translated by Wöhler), **1828**, III, 641. L. J. Thenard, "Traité de Chimie," **1835**, IV, 309. A. Ure, "Dictionary of Arts, Manufactures and Mines," **1848**, I, 357. U. S. patents 31,240 (1861) and 51,331 (1865). *Gummi-Ztg.*, **5**, 5 (1891). *J. Soc. Chem. Ind.*, **13**, 473 (1894); **24**, 1274 (1905). *Gummi-Ztg.*, **27**, 1388 (1913). *J. Russ. Phys.-Chem. Soc.*, **47**, 1898 (1915); **48**, 1114 (1916). U. S. patent 1,495,580 (1924).

[2] "Standard Methods," Inst. Petroleum Tech., 3rd Ed., **1935**, p. 187.

[3] *J. Soc. Chem. Ind.*, **54**, 266T (1935).

[4] Res. Assoc. Brit. Paint Colour and Varnish Manufrs., *Tech. Paper*, **73** (1936).

[5] *J. Am. Chem. Soc.*, **47**, 718 (1925).

[6] *Ind. Eng. Chem.*, **15**, 961 (1923).

[7] *Angew. Chem.*, **47**, 111 (1934).

[8] *Chem.-Ztg.*, **58**, 681 (1935).

[9] *Rev. Prod. Chim.*, **38**, 737 (1935); **39**, 4, 65 (1936).

[10] *Gummi-Ztg.*, **46**, 497 (1932).

[11] *Chemistry & Industry*, **1936**, 407.

[12] *Fuel*, **14**, 14, 56, 80 (1935).

[13] *Chem. Age*, **33**, 417 (1933).

[14] *Farben-Ztg.*, **40**, 860, 885, 909 (1935).

[15] *J. Text. Inst.*, **19**, 77, 389 (1928).

[16] *Paint Manuf.*, **7**, 157 (1937).

[17] *Bull. Rubber Growers' Assoc.*, **18**, 391 (1936).

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The Sensitive Detection of Organically Combined Bromine

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When a few drops of concentrated copper sulfate solution are added to a concentrated solution of potassium bromide, this solution turns yellow or brownish. When it is warmed, the color darkens, and on cooling or by dilution it becomes light again; finally at a definite concentration the color becomes yellow-green.

If a drop of the concentrated solution is placed on chemically pure filter paper and is allowed to dry, a bright or dark purple-red color is obtained, the shade depending on the method of drying. This color appears even when drying is at room temperature; it becomes paler when one breathes on the sample, and disappears completely when the colored spot is moistened with water, but on drying reappears as a pale rose color, the intensity of which depends on the concentration.

The same purple color, but more brilliant, appears when a few drops of concentrated sulfuric acid are added to potassium bromide–copper bromide solution. In this case the color is extraordinarily intense, and it is visible even when only 0.5 mg. of bromine per liter is present.

The best method of procedure is to place a few drops of the solution to be tested on a piece of chemically pure filter paper, allow to dry, and touch the spot with a glass rod moistened with sulfuric acid (1:1), whereby a distinct brown-violet ring is formed, even at the dilution mentioned above. The sulfuric acid plays only a secondary role in that it liberates hydrogen bromide from the potassium bromide; with copper bromide the hydrogen bromide then forms the complex compound mentioned. Chlorine ions do not destroy the color.

The reaction can, as a typical instance, be utilized for detecting small amounts of bromine present in rubber products treated with bromine. In this case, the procedure is to treat the rubber article with hot potassium hydroxide solution for a short time. The solution, filtered if necessary, is treated on a watch glass with a drop of copper sulfate solution (which gives a precipitate of cupric hydroxide) and then with one or two drops of concentrated sulfuric acid. Brominated rubber products give a distinct violet coloration. Traces of chlorine, attributable to the presence of white factice or to cold vulcanization, do not disturb the reaction, a fact naturally of great importance.

This purple color of a solution of $CuBr_2 . 4H_2O$ with hydrogen bromide has already been described by Sabatier (*Comptes rendus*, **118**, 980 (1894)), but since his time the phenomenon has apparently been forgotten. It probably depends on the formation of a cupric bromide–hydrogen bromide complex of the composition: $HCuBr_3$, or of salts of this complex, since also concentrated solutions of bromides (KBr, LiBr, etc.) give similar colors with the crystallized $CuBr_2.4H_2O$ compound. This would also serve to explain the appearance of the purple color by the mere drying of a concentrated solution of $KBr . CuBr_2$.

This reaction represents an equilibrium: $KBr + CuBr_2 \rightleftarrows KCuBr_3$, which depends to a considerable extent on the concentration and on the temperature. An increase in the concentration and also an increase in the temperature displace this equilibrium to the right.

In the case of the hydrogen bromide compound, the volatility of hydrogen bromide is an added factor. If it is expelled by heating, the coloration is destroyed, with accompanying separation of brown cupric bromide. The same effect is observed at room temperature if, after appearance of the purple color in the solution, a further quantity of concentrated sulfuric acid is added. The result of such an addition is to displace the equilibrium: $CuBr_2 + HBr \rightleftarrows HCuBr_3$, again to the left.

Cupric hydrogen bromide is unquestionably a coördinated compound, with coordination number 4, analogous to the cupriammonium 4. The unusually intense color is peculiar to these two complexes, and hence it may be used on the one hand for the colorimetric detection of the bromine ion, and on the other hand of the cupric ion, as in the latter case it has been used for so long.

Finally, the formation of the deep purple-red cupric hydrogen bromide complex can also be utilized as a sensitive means of detecting copper, in which case the procedure is similar to that used for detecting bromine on filter paper. In this way it is possible to identify unmistakably 0.05 mg. of cupric ion per liter by the formation of a brown-violet ring.

As far as the absorption spectrum of a dilute violet solution in a hand spectroscope is concerned, absorption in the various wave-lengths shows faint bands in the red at 6000 A. U., dark bands in the green between 5500 and 4400 A. U.; the violet end of the spectrum beyond 4400 A. U. is transmitted to a greater or less extent, depending on the intensity of the color.

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Properties of Sponge Rubber as a Material for Damping Vibration and Shock

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Summary

In order to obtain vibration-proof mountings, use is frequently made of sponge rubber. In this paper investigations are described concerning the factors on which its vibration damping properties depend. Formulas have been deduced for the mechanical impedance of sponge rubber, taking into account the presence of pores in the material. The formulas render the results of the measurements satisfactorily and, at the same time, they show how the qualities depend on factors such as porosity, kind of rubber, size of the pores, dimensions, etc. Under Section 6 we have examined more closely the choice of sponge rubber and the way of utilizing it in order to obtain the best results.

1. *General.*[1]—Sponge rubber appears to possess excellent qualities as a damping material. This being so, the question arises as to what part is played by the air it contains, and how this air content must be fixed to obtain the best results. We have attempted to answer this question by paying attention to the mechanical impedance of sponge rubber.

When sponge rubber is subjected to an external force, part of this force is expended in bringing about the elastic deformation of the rubber; another part is spent in compressing the air.

By this compression part of the air contained in the sponge is driven outwards through the pores. But this outward motion gives rise to friction, and therefore this displacement of air utilizes part of the external force to overcome resistance.

Owing to this behavior of sponge rubber, one can obviously substitute for it the diagrammatic arrangement shown in Fig. 1. This represents an air-filled cylinder with a weightless piston which moves without friction. The air inside the cylinder communicates with the outer air (pressure p_0) by means of a capillary (length l, radius R). In the cylinder an ideal spring (compliance c_r) is fitted. The spring, the air in the cylinder, and the capillary of this arrangement are, therefore, analogous to the rubber skeleton, the air content, and the pores of the sponge, respectively.

In deducing certain expressions for the mechanical impedance of the substitution scheme of Fig. 1 we avail ourselves of the calculus with complex quantities used in the theory of the alternating current. For greater simplicity, we first introduce the electrical analog to Fig. 1, from which the mechanical impedance can then readily be deduced.

The external force $F = F_m \cos \omega t$ is applied to the piston. This force must compress the steel spring and at the same time overcome the counter-pressure of the air inside the cylinder. We shall therefore have two impedances in series, one from the steel spring and one from the air. The steel spring is analogous to a condenser of impedance $1/j\omega c_r$ and the air is represented by an arrangement in parallel of a condenser (impedance $1/j\omega b$) and a resistance a. This is plausible if we consider that

the elastic compressibility of the air, as well as its outward flow, will cause a displacement of the piston. In this way we arrive at the electrical arrangement shown in Fig. 2.

The values for a and b are easily obtained from the expressions:

$$a = \frac{8\mu l O^2}{\pi R^4} \text{ and } b = \frac{\chi_0}{\chi p_0 O} \tag{1}$$

where μ = viscosity coefficient of air
O = area of the piston
χ_0 = average length of the air content
χ = Poisson's Constant

The expression for a was deduced with the aid of Poiseuille's law, and we refer to the assumption underlying this application under 4.

2. *Calculation of the Mechanical Impedance.*—For the mechanical impedance z we find:

$$z = \frac{1}{j\omega c_r} + \frac{a/j\omega b}{1/j\omega b + a} = \frac{1}{j\omega c_r} \cdot \left\{ \frac{(a^2b^2 + a^2bc_r)\omega + 1/\omega + jac_r}{a^2b^2\omega + 1/\omega} \right\} \tag{2}$$

from which we obtain for the angle of loss δ (angle of phase between force and deviation):

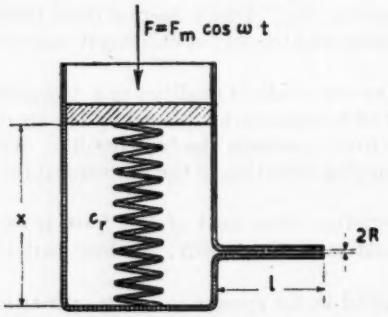

Figure 1—Substitution-Arrangement for Sponge Rubber

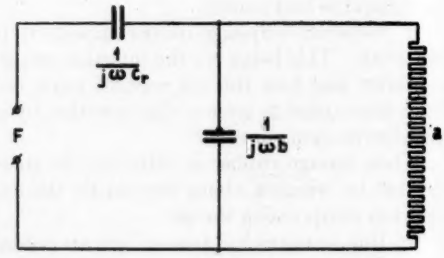

Figure 2—The Electrical Analog to Fig. 1

$$\tan \delta = \frac{ac_r}{(a^2b^2 + a^2bc_r)\omega + 1/\omega} \tag{3}$$

It appears therefore that as a function of ω, δ possesses a maximum, *viz.*, for:

$$1/\omega_0^2 = a^2b^2 + a^2bc_r \tag{4}$$

Denoting the maximum angle of loss by δ_0, we can write for (3):

$$\tan \delta = \frac{2 \operatorname{tg} \delta_0}{\omega/\omega_0 + \omega_0/\omega} \tag{5}$$

where

$$2 \tan \delta_0 = ac_r\omega_0 \tag{6}$$

The angle of loss depends therefore in a very simple way on the frequency, and vanishes for great and small values of ω.

The compressibility c of the system is found, by definition, by putting $1/j\omega c$ equal to the imaginary part of z (Equation 2), hence:

$$c = c_r \left\{ 1 - \frac{a^2b^2c_r}{a^2b^2 + a^2bc_r + 1/\omega^2} \right\} \tag{7}$$

Owing to the introduction of ω_0 and δ_0 we could write (3) in the form (5), thereby completely disposing of the quantities a, b, and c_r in this expression. We proceed in the same way with Expression 7. For, with the aid of (6) and (4) we find:

$$ab\omega_0 = \pm \sec \delta_0 - \tan \delta_0 \tag{8}$$

The minus sign in front of sec δ_0 having no physical meaning whatever, we can write for (7):

$$c = c_r \left\{1 - \frac{2}{1 + (\omega_0/\omega)^2} \cdot \frac{\sin \delta_0}{1 + \sin \delta_0}\right\} \tag{9}$$

3. *Graphical Representation of the Formulas Deduced Above.*—The introduction of the quantities δ_0 and ω_0 enables us to simplify the formulas considerably. Quantities like μ, l, O, R, x, χ_0 do not any longer enter explicitly into these expressions. This means a great simplification in the comparison of the formulas with the results of the measurements.

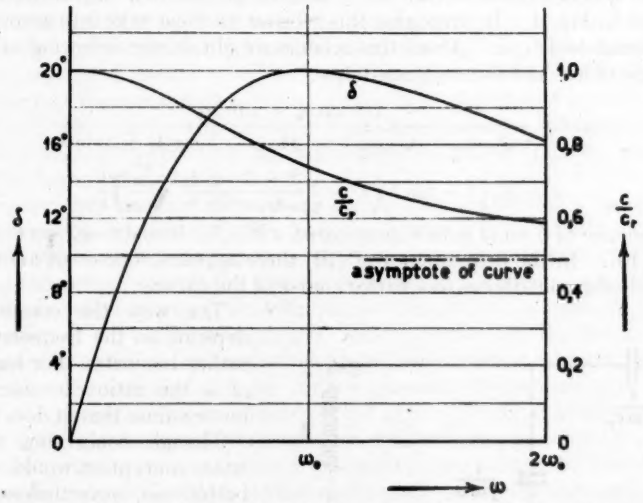

Figure 3—Theoretical Curves for Angle of Loss and Compliance (Assuming δ_0 20°)

The quantity x has also disappeared. It is, therefore, impossible to tell directly from the measuring results whether we have to deal with isothermal ($x = 1$) or adiabatic ($x = 1.4$) vibrations in the system. In calculating ω_0, x was tacitly assumed to be independent of the frequency, at least for values of ω in the neighborhood of $\omega = \omega_0$. For small or high frequencies we must however put x equal to 1 and to 1.4, respectively. For intermediate frequencies x will gradually increase from 1 to 1.4, but it is impossible to say beforehand in which frequency region this increase will take place. It is only when this region also comprises $\omega = \omega_0$, that the influence of this change of x on the results will be clearly perceptible.

In Fig. 3 the change of c and δ with the frequency is represented for $\delta_0 = 20°$. For $\omega \gg \omega_0$, δ approaches hyperbolically towards zero, whereas c/c_r approaches asymptotically towards a finite value, namely:

$$(c/c_r) \sim = \frac{1 - \sin \delta_0}{1 + \sin \delta_0}$$

4. *Discussion of the Formulas.*—In deducing the formulas, the contribution of the pores to the impedance was assumed to be purely in the nature of a resistance. But this assumption is questionable. The problem is, namely, more or less analogous to that of the reflection and absorption of sound waves by porous substances. For that reason the honeycomb wall theory of Rayleigh might assist in this matter.[2]

When a pressure difference Δp is applied to a capillary, the steady state of motion does not set in instantaneously. A propagation velocity of the pressure disturbances comes into play, which, however, depends on the frequency. Owing to the frictional forces in the capillary, such vibrations are very strongly damped. That is why, on applying a sine-like variation of pressure to the end of a very long capillary, a state of motion will be set up which is restricted to a very short length of the capillary. At greater distances from the end the disturbances are hardly perceptible. In this case the impedance is not purely of the nature of a resistance, but is built up of two parts, one of capacity and one of resistance, the impedances of which are equal and inversely proportional to $\sqrt{\omega}$.

By these considerations we are led to assume an electrical substitution scheme arranged as in Fig. 4. In arranging this scheme we must take into account that a is proportional to $1/\sqrt{\omega}$. From this scheme we obtain the following expressions for the angle of loss and the compressibility:

$$\tan\delta = \frac{\sqrt{2}\sin\delta_0 + \sin 2\delta_0}{(\sqrt{\omega/\omega_0} + \sqrt{\omega_0/\omega})\cos 2\delta_0 + \sqrt{2}\cos\delta_0 + 2\sin\delta_0} \tag{10}$$

$$c = c_r\left\{1 - \tan\delta\left(1 + \frac{\sqrt{2} - 2\sin\delta_0}{\cos\delta_0 + \sin\delta_0}\sqrt{\frac{\omega}{\omega_0}}\right)\right\} \tag{11}$$

The dependence of δ on ω is now (compared with (5)) less strong, since only $\sqrt{\omega}$ enters in (10). In the denominator of (10) there appears, moreover, another constant, which also contributes to a flatter course of the curve.

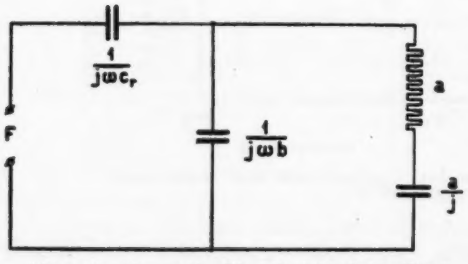

Figure 4– Alternative Electrical Analog to Fig. 1

The way the compressibility depends on the frequency is now rather intricate. For high values of ω the ratio c/c_r decreases to lower values than it does in (9).

Though concerning this, our latter conception would seem the better one, nevertheless, there is reason to consider the former conception the better one, for, in reality, the pores are not infinitely long, as they are supposed to be in the treatment of the problem of the honeycomb wall.

5. *Measurements.*[3]—Figure 5 shows a few of the results of measurements. The material in question was a sponge of dimensions $11.4 \times 7.3 \times 3.8$ cm.^{3} and with very narrow pores. The weight of the rubber amounted to 74 grams. The free volume of the pores was estimated at 70 per cent. The static load under which the experiments were carried out was 0.14×10^6 dyne per sq. cm. (≈ 0.14 atm.).

On comparing the results in Fig. 5 with the theoretical results in Fig. 3, we conclude that the qualitative agreement is very satisfactory. Indeed, closer agreement was not to be expected, starting, as we did, from so simple a substitution scheme as Fig. 1.

δ_0 amounts to about 20°. Combining (6) with (8) and (1) yields for δ_0 the expression:

$$\tan \delta_0 = \frac{c_r x p_0 O/\chi_0}{2\sqrt{1 + c_r x p_0 O/\chi_0}} \qquad (12)$$

As can be seen from Fig. 5, for very low frequencies the compliance $c = c_r \approx 350 \times 10^{-10}$. In connection with the dimensions of the sponge, we take for O the area 11.4×7.3 cm.^{2}. p_0 is the atmospheric pressure. Taking into account the porosity of 70 per cent, we put: $\chi_0 = 0.7 \times 3.8$. For $x = 1$, substitution of these various values in (12) gives for δ_0 the value of 20.9°. This is another surprisingly good agreement. It would, of course, be stretching the point too far to conclude from this that the vibrations are indeed isothermal.

Figure 3 was drawn on the assumption that the rubber is free of loss. This is, however, not quite true. Presumably the angle of loss of the rubber will amount to a few degrees. For that reason the curve for δ in Fig. 5 will not pass through the origin.

One more good agreement between Figs. 3 and 5 is the following. Once δ_0 and ω_0 are chosen, Fig. 3 is completely determined. Therefore the rate of decrease of c/c_r when ω increases from 0 to ∞ is also determined by δ_0 and ω_0. And on this point too, the agreement is most satisfactory, although for high values of ω the measured ratio c/c_r decreases to values lower than the computed ones. This would point to the fact that, to a certain extent, a process similar to that in the honeycomb problem does take place. On the other hand, the measured change of δ with the frequency is slightly steeper than the computed one, instead of flatter, and this contradicts the honeycomb theory.

6. *Requirements for Good Vibration Damping, from the Point of View of Assigning the Most Favorable Dimensions to the Damping Material.*—Elastically mounted systems are of very frequent occurrence. They are so mounted with a view either to insulating the system against the vibrations of the foundation or, more often, to insulating the foundation against the vibrations of the system (for example, machines).

The quality of the elastic mounting is chiefly governed by the mutual positions (on a frequency scale) of the frequencies to be insulated (for example, the number of revolutions of a machine) and the various resonance frequencies of the vibrating system. Neglecting the slight influence of the angle of loss on the latter frequencies, the vertical translation-resonance frequency is determined by $\omega = 1/\sqrt{mc}$ (m = mass of the system, c = compliance of the springs supporting the system). Altogether, we have to deal with 6 resonance frequencies (3 rotations and 3 translations!). As a rule these frequencies have values lower than $\omega = 1/\sqrt{mc}$, and the mounting will be the better, the further $\omega = 1/\sqrt{mc}$ is below the frequencies to be insulated. In the reverse case the effect on the mounting will be unfavorable. Usually a high value of the compliance c will be necessary to make the resonance frequencies sufficiently low.[4]

The angle of loss plays an important part in the following cases, for example:

(*a*) During the period of acceleration of an elastically mounted machine from starting speed to its normal working speed. In passing the various resonance frequencies, the deviation is restricted mainly by the existence of the angle of loss.

(*b*) When mechanical shocks occur. The quicker these are damped, the greater are the losses.

In both cases a fairly large angle of loss is demanded, more in particular however for frequencies of the order of the resonance frequencies, which will mostly lie in the neighborhood of 200–300 r. p. m.

When sponge rubber is used as an elastic layer, we should endeavor to make the maximum angle of loss fall within the region of the resonance frequencies, since

otherwise the losses would be a disadvantage rather than an advantage. It is, therefore, a matter of importance to investigate how far the value and the (frequency) position of the maximum angle of loss δ_0 can be influenced favorably by the choice of the qualities of the material.

Equation 12 shows at once how δ_0 depends on the qualities of the material. Equation 6 together with (1) and (12) gives a similar expression for ω_0, namely:

$$\omega_0 = \frac{\pi R^4 x p_0}{8\mu l O \chi_0 \sqrt{1 + c_r x p_0 O/\chi_0}} \qquad (13)$$

A close study of the influence of the various qualities of the material (represented, for example, by R, O, χ_0, c_r) on δ_0 and ω_0 leads to the following conclusions:

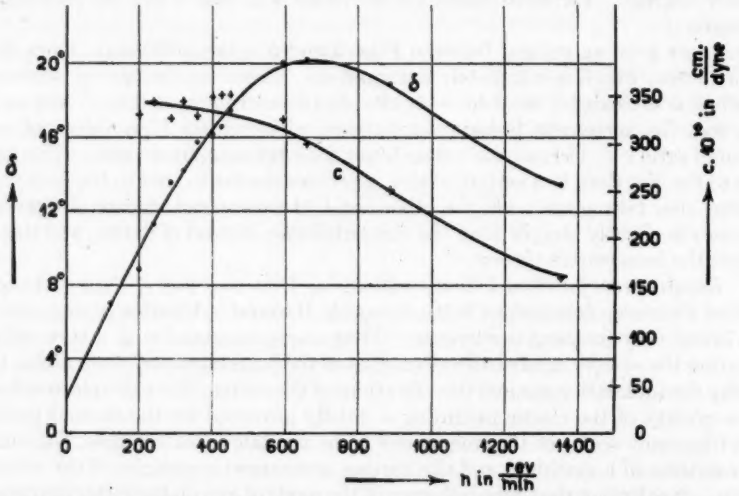

Figure 5—Measured Values for Angle of Loss and Compliance (Compare Fig. 3)

(*a*) δ_0 is only slightly or negligibly dependent on the sponge-area O, the thickness of the sponge, and the fineness of the pores (the air content remaining constant). This is easily deduced from (12).

(*b*) δ_0 increases with increasing compressibility of the rubber and with increasing porosity (the fineness of the pores remaining constant). (This follows from (12).)

(*c*) ω_0 is only slightly or negligibly dependent on the thickness and area of the sponge (see (13)).

(*d*) ω_0 increases slightly with decreasing porosity (the fineness of the pores remaining constant) and with decreasing compressibility of the rubber.

ω_0 depends strongly on the fineness of the pores (the porosity remaining constant). Presumably ω_0 will increase nearly proportionally to the square of the average width of the pore. In (13) R enters as R^4 and the number of pores must be made proportional to R^2, as porosity is kept constant.

Our conclusion, from a rubber technological point of view, is therefore that for vibration-damping purposes sponge rubber should consist of soft rubber, possess great porosity, and, in particular, very fine pores.

The best way, however, of applying the sponge rubber is to treat each case individually and to choose the qualities in accordance with requirements.

References

[1] For definitions and introductory remarks, see C. W. Kosten and C. Zwikker, *Physica*, **4** [3], 221 (1937).

[2] Crandall, "Theory of Vibrating Systems and Sound," London, **1927**, p. 186.

[3] For a description of the measuring apparatus, see C. W. Kosten and C. Zwikker, *loc. cit.*

[4] Knudsen, "Architectural Acoustics," New York, **1932**, p. 270. *Schmidt, Gesundh.-Ing.*, **46**, 61 (1923). Davis, "Modern Acoustics," London, **1934**, p. 24. Föppl, "Aufschaukelung und Dämpfung von Schwingungen," Berlin, **1936**. Thum und Oeser, "Gummifederungen für ortefeste Maschinen," Berlin, **1935**, p. 24.

[Translated by Charles Blanc for Rubber Chemistry and Technology from Caoutchouc and Rubber (U. S. S. R.), pages 29–31, No. 7, July, 1938.]

Formula for Determining the Viscosity of Latex

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Jordan, Brass, and Roe have published an article entitled "Examination of Rubber Latex and Rubber Latex Compounds. I. Physical Testing Methods" (*Ind. Eng. Chem., Anal. Ed.*, **9**, 182–189 (1937); Rubber Chem. and Tech., **10**, 615 (1937)). A part of the work is devoted to measurements of the viscosity of latex by the capillary-flow method.

When working with moderately viscous liquids, the authors used the common burette apparatus, in which the liquid flows by its own hydrostatic pressure. With highly viscous liquids they applied additional air pressure, with corresponding changes in the apparatus as a whole. In the second case, the authors made use of the following basic formula for calculating the limiting coefficient of viscosity η':

$$\eta' = K \frac{\{d_{Hg}(w_2P_1 - w_1P_2) + d_1(w_2h_1 - w_1h_2)\}}{w_1w_2} \times \frac{t_1t_2}{(t_2 - t_1)} d_1 \qquad (1)$$

where K is the apparatus constant, depending on the length and radius of the capillary, d_{Hg} and d_1 are the densities of mercury and latex (in gram per 1 sq. cm.), t_1 and t_2 are the times of efflux (in sec.), P_1 and P_2 are the air pressures (in cm. of Hg) for two separate measurements, h_1 and h_2 are the mean heights (cm.) of the latex column over the lower end of the capillary at the pressures P_1 and P_2, and w_1 and w_2 are the amounts (in g.) of latex flowing at pressures P_1 and P_2 for times t_1 and t_2.

Formula 1 is highly inconvenient for use in the calculations, because for each determination of η' 13 multiplication–division and 4 addition–subtraction calculations are required. The formula is not only cumbersome, but is also incorrect. This becomes evident even in the most ordinary case with the determination of different amounts of latex for the same periods of time ($t_1 = t_2$), where η' becomes equal to infinity, which is absurd. The incorrectness of the formula is a result of a serious mathematical error by the authors. Though the development of the formula is not given in the article, the source of the error can be easily traced, as follows.

As is well known, in the case of a Newtonian liquid, *e. g.*, water, the coefficient of viscosity η is directly proportional to the ratio of the displacing force F and the degree of displacement v:

$$\eta = K \frac{F}{v} \qquad (2)$$

where K is the same constant as in Formula 1.

F is equal to the total pressure on the effluent liquid, *i. e.*, it is equal to the sum of the hydrostatic pressure of the liquid itself, hd_1, and the additional air pressure, Pd_{Hg}, where h and P are the heights of the columns of the liquid and mercury, respectively, and d_1 and d_{Hg} are their densities:

$$F = (hd_1 + Pd_{Hg}) \qquad (3)$$

The magnitude v is equal to the velocity of flow of the liquid, *i. e.*, it is equal to the volume of liquid flowing in 1 sec.:

$$v = \frac{V}{t}$$

where V is the volume of liquid flowing in t sec. By replacing volume V by the weight w:

$$V = \frac{w}{d_1}$$

we obtain:

$$v = \frac{w}{td_1} \tag{4}$$

By substituting F (3) and v (4), found experimentally, in (2), we obtain:

$$\eta = K \frac{hd_1 + Pd_{Hg}}{w} \times td_1 \tag{5}$$

In the case of a Newtonian liquid, *e. g.*, latex, the limiting coefficient of viscosity η' becomes directly proportional to the ratio of the two differences: the difference of the displacing forces F_1 and F_2 to the difference of the corresponding degrees of displacement v_1 and v_2:

$$\eta' = K \frac{F_1 - F_2}{v_1 - v_2} \tag{6}$$

Taking Expressions 3 and 4 and substituting F_1, F_2, v_1, and v_2 in (6), we obtain:

$$\eta' = K \frac{(h_1d_1 + P_1d_{Hg}) - (h_2d_1 + P_2d_{Hg})}{w_1/t_1 - w_2/t_2} \times d_1 \tag{7}$$

By simple conversion, we obtain:

$$\eta' = \frac{K\,(h_1d_1 + p_1d_{Hg}) - (h_2d_1 + P_2d_{Hg})}{w_1t_2 - w_2t_1} \times t_1t_2d_1 \tag{8}$$

This formula is basically different from Formula 1, proposed by the American investigators.

TABLE I

COMPUTATION OF HYDROSTATIC PRESSURE OF LATEX IN CENTIMETERS OF MERCURY

Latex Column Height h (Cm.)	Corresponds to the Hg Column p Cm. at the Latex Density d_1					
	0.9–0.92	0.9–0.94	0.94–0.96	0.96–0.98	0.98–1.00	1.00
0–2	0.067	0.069	0.07	0.072	0.073	0.074
2–4	0.2	0.21	0.21	0.22	0.22	0.22
4–6	0.33	0.34	0.35	0.36	0.37	0.37
6–8	0.47	0.48	0.49	0.50	0.51	0.52
8–10	0.60	0.62	0.63	0.64	0.66	0.67
10–12	0.74	0.76	0.77	0.79	0.80	0.81
12–14	0.87	0.89	0.91	0.93	0.95	0.96
14–16	1.01	1.03	1.05	1.07	1.09	1.11
16–18	1.14	1.17	1.19	1.22	1.24	1.25
18–20	1.27	1.30	1.33	1.36	1.39	1.40
20–22	1.41	1.44	1.47	1.50	1.53	1.55
22–24	1.51	1.58	1.61	1.65	1.68	1.70
24–26	1.68	1.72	1.75	1.79	1.83	1.85
26–28	1.81	1.85	1.89	1.93	1.97	1.99
28–30	1.95	1.99	2.04	2.08	2.12	2.14

If $t_1 = t_2$, Formula 8 becomes:

$$\eta' = K \frac{(h_1d_1 + P_1d_{Hg}) - (h_2d_1 + P_2d_{Hg})}{(w_1 - w_2)} \times td_1 \tag{9}$$

To make the calculation more convenient, h_1d_1 (hydrostatic pressure of latex column) can be expressed as p cm. of mercury. Then for the total pressure we obtain $(p_1 + P_1)d_{Hg}$ instead of $h_1d_1 + P_1d_{Hg}$, and correspondingly $(p_2 + P_2)d_{Hg}$ instead of $h_2d_1 + P_2d_{Hg}$.

By substituting the new expressions of the total pressure in (9), we finally obtain:

$$\eta' = K \frac{(p_1 + P_1) - (p_2 + P_2)}{(w_1 - w_2)} \times d_{Hg}d_1t \qquad (10)$$

Formula 10 is very simple and convenient in making calculations.

The preceding table can be used in computing the hydrostatic pressure hd_1 in cm. of mercury.

Returning to Formula 1, it can be assumed that the mistake occurred as a result of the authors' incorrect transcription of the original expression (7) into the following form:

$$\eta' = K \frac{\frac{(h_1d_1 + P_1d_{Hg})}{w_1} - \frac{(h_2d_1 + p_2d_{HG})}{w_2}}{\frac{1}{t_1} - \frac{1}{t_2}} \times d_1 \qquad (11)$$

It can be readily seen that their basic Formula 1 is obtained by simple conversion of Equation 11.

However, it is obvious that Expressions 11 and 7 are not the same. It is also obvious that with different weights w_1 and w_2 of the effluent liquid, $\frac{1}{t_1}$ and $\frac{1}{t_2}$ do not represent degrees of displacement, and are not even proportional to them. Likewise, $\frac{h_1d_1 + P_1d_{Hg}}{w_1}$ and $\frac{h_2d_1 + P_2d_{Hg}}{w_2}$ do not represent the displacing forces.

Therefore, Expression 11 and Formula 1 derived from them are devoid of any physical meaning and cannot be applied to the determination of the viscosity of latex.

In their place, Formulas 8, 9, and 10 should be used.

Analysis of Organic Accelerators

J. G. Robinson

CORRECTION

In an article entitled "Analysis of Organic Accelerators" by J. G. Robinson, which was published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. XI, No. 4, pages 728–739 (October, 1938), a correction is to be made in line 3 of page 738.

The concentration of hydrochloric acid should be 2-normal, not 0.5-normal. The sentence should therefore read: "Boil gently till dissolved, then cool and add, with continuous stirring, 25 cc. of 2 *N* hydrochloric acid and boil for about 10 minutes to remove hydrogen sulfide and to coagulate the sulfur."

The procedure will not work successfully with 0.5 *N* hydrochloric acid.